IRON AND STEEL
INSTITUTE PAPERS

PLANT DESIGN · MANUFACTURE · RESEARCH · DEVELOPMENT

Effect of Annealing on the Resistance of Galvanized Steel to Atmospheric Corrosion

By S. E. Hadden, A.I.M.

SYNOPSIS

Experimental work is described showing that by annealing hot-dipped galvanized wires and sheets the resistance to atmospheric corrosion in Central London was substantially increased. In the case of wires, the longest life was more than three times that of an unannealed wire, and was obtained by annealing at 650° C. for 30 min., the average iron content of the coating being 21·6%. The percentage of iron in the coatings increased with both time and temperature of annealing, and the annealed coatings consisted solely of zinc–iron alloys, the outer zinc layer of the hot-dipped coating having disappeared during the annealing process. For wires with coatings containing 10–21·6% of iron the life of the coatings and the residual strength of the wires at the end of the test were greater as the iron content increased.

The appearance during exposure is described and suggestions are made to account for the enhanced protection against corrosion afforded by annealing.

Introduction

THE resistance to corrosion, under urban atmospheric conditions, of ordinary hot-dipped galvanized steel was compared with that of similar material annealed at temperatures of 450–650° C. Wires and sheets were exposed to the central London atmosphere and their changing condition is described, the test being continued until most of the specimens had rusted over their whole surfaces. Some of the annealing treatments greatly extended the life of hot-dipped coatings. An attempt was also made to compare the corrosion resistance of the various layers in an ordinary hot-dipped coating, but the seasonal variation of atmospheric conditions prevented any exact comparison.

The resistance to atmospheric corrosion of zinc coatings containing up to about 10% of iron is approximately proportional to the thickness of the coating and is independent of the method of application. Hudson and Banfield[1] provide good evidence for this in tests at Sheffield on coatings produced by hot-dipping, electrodeposition, spraying, and cementation (sherardizing). Only coatings containing more than 10% of iron showed improved corrosion resistance in the present work.

Storey[2] reports that sherardized coatings containing 15–20% or more iron were usually less resistant to weathering than those containing less iron. He observes that zinc-rich zinc–iron alloys exposed to the atmosphere will usually turn a deep grey and finally black. Sometimes they turn a pale yellow or red which becomes darker and then black. He states that "this black coating is supposed to be the magnetic oxide of iron. Sherardizing, which has this surface formation, becomes highly resistant to further corrosion. But this magnetic oxide is not formed in all cases."

Schueler[3] describes a new method of coating wire with zinc, termed 'galvannealing,' which consists of heat-treating after hot-dipping so that the average iron content of the coating is raised to between 7·1–8·5%. He claims that this treatment gave smooth, flexible, and malleable coatings, and increased the corrosion resistance. He also states that the iron content of the coating could be increased to as much as 32% by suitable heat-treatment, but coatings with over 10% of iron resisted atmospheric corrosion less well than those with lower iron contents.

Since the present results were obtained, more extensive exposure tests on annealed zinc-coated specimens have been started in a collaborative research by the British Iron and Steel Research

Manuscript received 22nd June, 1951.

Mr. Hadden is a Research Assistant with the British Non-Ferrous Metals Research Association, London.

The work described in this paper was made available to members of the B.N.F.M.R.A. in a confidential research report issued in April, 1951.

Table I

MATERIALS USED IN ATMOSPHERIC CORROSION TESTS

Material	Mark	Description	Wt. of Coating, oz./sq. ft.	S.W.G.	Impurities in Coating (Spectrographic Analyses), approx. %					
					Pb	Cd	Cu	Al	Sn	Mg
Wire	MHZ	Hard drawn hot-dipped galvanized steel	0·97	12	1	0·001	>0·1	<0·001 if any	<0·01 if any	< 0·003 if any
Sheet	JQX	Hot-dipped galvanized steel	0·62	21	1	0·1	0·1	<0·001 if any	0·1	< 0·003 if any
Sheet	PAL	,, ,, ,,	1·4	22	...	...	...	...	...	...

Association, and the British Non-Ferrous Metals Research Association.

MATERIALS

Details of the commercially produced galvanized wire and of two batches of sheet used for some subsidiary experiments are given in Table I.

The sheets of Mark PAL were made by dipping small mild-steel sheets in a pure zinc bath to which had been added 1% of lead and 0·1% of tin.

The analysis of the basis steel of the wire was: 0·51% carbon, 0·79% manganese, 0·13% silicon, 0·073% copper, 0·056% nickel, and 0·023% sulphur.

EFFECT OF ANNEALING ON THE PROPERTIES OF GALVANIZED STEEL WIRE

Structure and Composition of Coatings

Wires were annealed for various times and temperatures in an atmosphere of air, using an electrically heated muffle furnace. Some were then electrolytically stripped using the method described by Britton,[4] the current density being 1 amp./sq. in. corresponding to a uniform rate of dissolution of the coating of about 0·1 oz./sq. ft./min. Voltage/time curves for some of the specimens are shown in Fig. 1. A change in the value of the voltage across the cell indicates a change in the composition of the coating at the corresponding point during the dissolution process.

Thus, on the curve of the as-received wire the voltage from 1 to 4 min. was constant while the outer zinc layer was being removed. From 5 to 9 min. the voltage rose during the removal of the alloy layers.

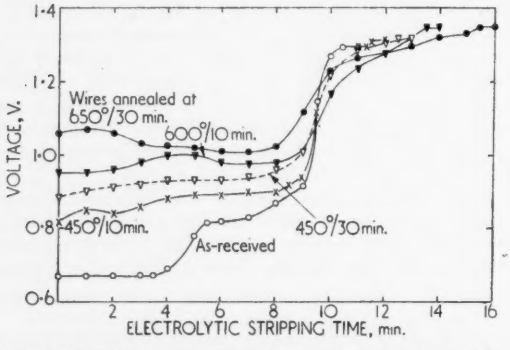


Fig. 1—Voltage/time curves of as-received and annealed galvanized steel wires electrolytically stripped at 1 amp./sq. in. (1 min. stripping removes approx. 0·1 oz./sq. ft. of coating)

Annealing for 10 min. at 450° C. apparently causes the unalloyed layer to disappear completely; annealing for longer times at 450° C. causes a progressive increase in the iron content of the coating, which tends to assume a more uniform composition. For higher temperatures of annealing the stripping voltage increases, further indicating a greater proportion of iron in the coating. The end point when all the coating is removed, as shown by the rise in voltage between 9 to 10 min. stripping, is sharp for the unannealed coating but is less sharp on annealed coatings, indicating that the zone with a very high iron content near the steel becomes thicker as the degree of annealing is increased.

The average percentage of iron in the annealed coatings as determined by stripping in inhibited acid and analysing the resulting solution is shown in Fig. 2, the figure for the unannealed coating being 4·2%. The stripping acid used was prepared by dissolving 2 g. of As_2O_3 in 50 ml. of sulphuric acid and making up to 1 l. with water.

Micrographs of annealed coatings are shown in Fig. 3. Between the coating annealed at 650° C. for 30 min. (Fig. 3*a*) and the unetched basis steel is a light-coloured layer, which appears to be the α solid

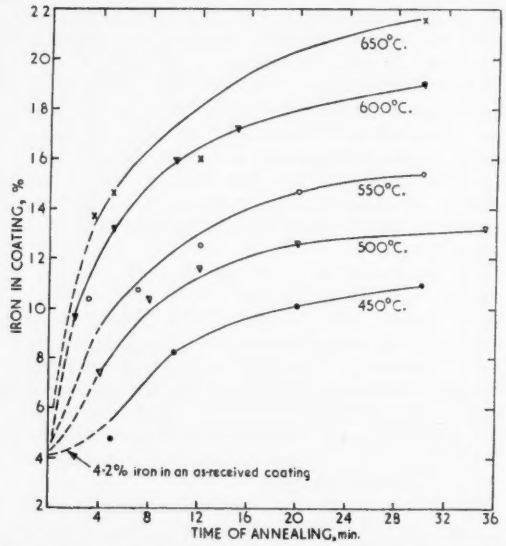


Fig. 2—Average iron content of coatings on galvanized steel wires after annealing at various temperatures.

solution of zinc in iron,[5, 6] insoluble in the stripping acid. Figure 3*b* shows the same annealed wire after stripping, with the α solid solution still remaining; within it are particles of the iron-rich γ phase, which is also insoluble. Wires stripped so that only these two phases remained were exposed to the atmosphere on the Euston Street roof and red rust was formed in 7 weeks. Hence this layer can hardly be regarded as a significant part of the protective coating. The rest of the coating consists of a zinc–iron alloy of granular appearance—probably the zinc-rich Γ' phase. Figure 3*c* reveals several alloy layers. The broken-up outer layer probably contains zinc and iron oxides formed during annealing and incompletely removed by the 10-sec. dip in 5% sulphuric acid given after annealing. The phases insoluble in the stripping acid were not formed at this temperature.

Mechanical Properties

The effect of annealing on the mechanical properties of the wires is shown in Table II : the ultimate tensile strength was lowered, and at temperatures of 600° C. and over the elongation of the wire increased, the effect being more marked at the higher temperatures.

The effect on the ductility of the coating was tested by bending the wires round a series of steel formers. The unannealed wire showed only very slight cracking on the outside of the bend on being bent round a former of approximately its own diameter. Coatings on wires annealed at 450–650° C. for 30 min. all crumbled on the inside of the bend when bent round a former of 0·6 in. dia. or less. The crumbling became severe, and some of the top layer of the coating was lost when the wire was bent round a former of 0·236 in. dia., but even with this severe test a considerable amount of coating still remained.

MAIN SETS OF TESTS

Details of Specimens and the Exposure

The specimens may be divided into three groups :

(i) Wires annealed at each of the temperatures and times shown in the first column of Table IV. After annealing these were dipped in 5% sulphuric acid for 10 sec. to remove annealing scale, and then washed with water

(ii) As-received wires, and similar wires electrolytically stripped at successive intervals from 1 to 8 min., thus exposing successive layers of the coating. These were rubbed free from electrolytic sludge and were washed with water

(iii) Wires annealed at 450° C. for 30 min. and then electrolytically stripped for the same periods as the unannealed wires. These received the 5% sulphuric acid dip after annealing, and after stripping were cleaned of sludge.

All wires were finally degreased with benzene and cut into 7-in. lengths. The ends were dipped in molten Chatterton's compound to a length of $\frac{3}{4}$ in., leaving $5\frac{1}{2}$ in. exposed. They were fixed by their ends into china cleats screwed to a wooden frame so that the wires were inclined at an angle of 30° to the horizontal, 3 ft. from the flat roof of the British Non-Ferrous Metals Research Association building in Euston Street. Duplicate specimens were fully exposed to the rain and weather, facing south-west. The test was in progress from 20th March, 1940 until 7th November, 1949 (503 weeks) when all but two of the wires had failed.

Table II

EFFECT OF ANNEALING ON MECHANICAL STRENGTH OF GALVANIZED HARD-DRAWN STEEL WIRE MHZ

Wire		Breaking Load, tons	U.T.S., tons/sq. in.	Elongation on 8 in., %
Untreated	1	0·848	89·3	6·9
	2	0·853	90·0	6·8
	3	0·850	89·5	6·9
Annealed:				
450° C./30 min.	1	0·759	80·0	6·3
	2	0·756	79·7	6·1
500° C./30 min.	1	0·693	73·0	5·8
	2	0·696	73·3	6·1
550° C./30 min.	1	0·621	65·5	6·2
	2	0·619	65·2	6·4
600° C./30 min.	1	0·548	57·7	7·3
	2	0·547	57·6	7·4
650° C./30 min.	1	0·464	48·9	9·0
	2	0·461	48·3	9·0

The criterion of failure of the coating was the appearance of a rough red rust patch of about $\frac{1}{10}$ in. in length, as this was found to indicate attack of the basis steel by pitting. No notice was taken of attack less than $\frac{1}{4}$ in. from the ends. The time taken for failure is called the 'life.' All the wires remained exposed for the whole 503 weeks, and comparison was then made of their residual strengths. Observations were made weekly during the first six months, and thereafter at least once a month.

Appearance During Test and Comparison of As-Received and Annealed Wires

During the period before failure it was found necessary to distinguish between the red rust of the basis metal (indicating failure) and the superficial yellow rust of the zinc–iron alloy. After the first rusting of the basis metal, its progress was noted until it covered the whole of the surface.

All the coatings developed yellow rust, but in the

Table III

AS-RECEIVED AND ANNEALED GALVANIZED STEEL WIRES : TIME FOR APPEARANCE OF YELLOW RUST AND THE BLACK LAYER

Temp. and Time of Annealing	Average Iron Content of Coating, %	Time (weeks) for Appearance of		Life, weeks
		Yellow Rust	Black Layer	
As-received	4·2	113	147*	159
450° C./30 min.	10·9	44	75	166
500° C./20 min.	12·6	46	75	168
550° C./30 min.	15·4	2	53	221
600° C./20 min.	18·0	1	75	253
650° C./30 min.	21·6	1	53	>503

* Slight blackening only

Table IV

LIFE UNDER URBAN ATMOSPHERIC CONDITIONS OF GALVANIZED STEEL WIRES ANNEALED FOR VARIOUS TIMES AND AT VARIOUS TEMPERATURES

Annealing		Average Iron Content of Coating, %[1]	Life (with Average of Duplicate Specimens), weeks		Excess Life due to Annealing, weeks	Time for 100% Red Rust, weeks[1]
Temp., °C.	Time, min.					
As-received	...	4·2	154, 164	159	...	179
450	5	4·8	150, 154	152	...	169
,,	10	8·2	150, 154	152	...	176
,,	20	10·1	154, 158	156	...	185
,,	30	10·9	164, 168	166	7	193
500	5	8·2	154, 162	158	...	181
,,	10	10·6	158, 169	164	5	198
,,	20	12·6	164, 172	168	9	188
550	5	10·0	167, 172	170	11	224
,,	10	12·4	172, 181	177	18	234
,,	20	14·7	190, 206	198	39	236
,,	30	15·4	216, 225	221	62	278
600	5	13·2	185, 187	186	27	259
,,	10	15·9	220, 232	226	67	271
,,	20	18·0	244, 262	253	94	360[3]
650	5	14·6	228, 257	243	84	380
,,	10	17·4	262, 290	276	117	388[3]
,,	20	20·4	430[4]	430	271	>503
,,	30	21·6	>503, >503	>503[5]	>344	>503

[1] In some cases interpolated from Fig. 2
[2] Average for two specimens
[3] Single specimens, the duplicates being taken from test after failure for examination of residual coating
[4] Single specimen—the duplicate specimen was taken from test before failure for examination of black film
[5] Neither specimen had failed at the end of the test

case of the annealed coatings, the appearance gradually changed to a uniform dark-grey or black colour. This appeared only to a slight extent on the as-received coatings. Tiny rust specks later appeared in the black layer, but investigation showed that a layer of coating remained under the rust specks, and that the steel was not pitted.

The early appearance of yellow rust does not indicate a rapid rate of corrosion, but only shows that the outer layers of an annealed specimen contain a greater proportion of iron than the similar layers of an unannealed specimen. This means an early loss of good appearance which might be commercially important, but Table III shows that for most of their lives the annealed coatings were covered with the smooth and uniform black layer, the appearance of which is not unpleasing.

RESULTS OF MAIN SET OF TESTS

Increase of Life of Hot-Dipped Coatings Obtained by Annealing

Table IV gives the times for failure and for complete destruction of the coatings for as-received and annealed wires. In addition to the wires shown in this table an unannealed wire and one annealed at 650° C. for 30 min., both electrolytically stripped to the basis steel, were exposed. Both completely rusted in five days.

The life did not begin to increase until the coating contained more than about 10% of iron, but thereafter it increased at an increasing rate with successively higher iron contents. The maximum increase, to a value more than three times the life of an as-received wire, was obtained with the wires annealed at 650° C. for 30 min. and containing 21·6% of iron. Failure of the annealed coatings did not occur until almost all the coating had disappeared. The residual coatings in the two unfailed specimens annealed at 650° C. for 30 min. were found to be 2% and 1·2% of the original weight of coating respectively. The longer life of the annealed coatings is not due to a greater total weight of coating by the interdiffusion of the basis iron and zinc, for the increase in weight of coating due to this cause is largely offset by loss due to oxidation of the zinc on annealing, the oxide produced being removed

(a) Hot-dipped galvanized wire MHZ, annealed at 650 C. for 30 min.

(b) Wire illustrated at (*a*), after removing coating by stripping acid

(c) Hot-dipped galvanized sheet JQX, annealed at 550°C. for 45 min.

Fig. 3—Microphotographs of annealed hot-dipped galvanized coatings × 500

(a) Uncorroded as-received wires for comparison
(b) Corroded as-received wires
(c) Corroded wires annealed 550°C. for 30 min.
(d) Corroded wires annealed 650°C. for 80 min.

Fig. 4—Appearance (after cleaning) of galvanized wires after 503 weeks' exposure to atmospheric corrosion (Actual size)

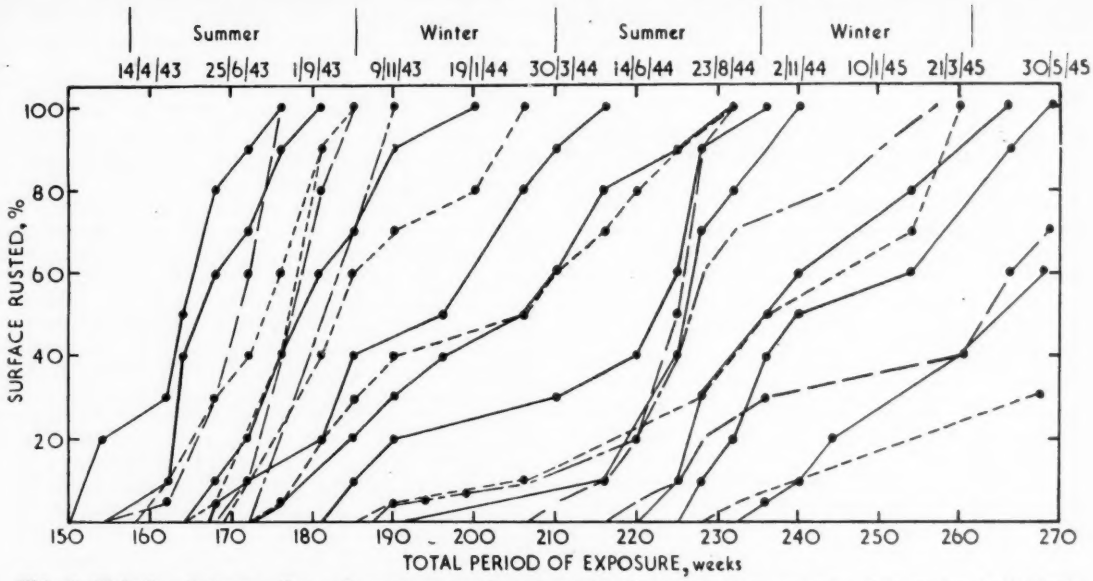


Fig. 5—Relation between time of exposure and percentage of surface area rusted. Curves for individual annealed wires with coatings having average iron content of 8–16%

by the acid dip. As a result, the annealed wires tested had a coating weight of at most 8% greater than that of the as-received wire.

The difference between the figures in columns 4 and 6 gives the time, after its first appearance, taken for rust to spread over the whole surface. This was longer for the annealed than for the as-received wires, and became longer as the percentage of iron in the coating increased. Hence the improved corrosion resistance of the annealed wires is greater than is represented by the figures in column 5.

In Fig. 5 the percentage of the surface rusted is plotted against the time of exposure for individua annealed wires with coatings containing 8–16% of iron. A seasonal variation in the rate of corrosion is apparent, with retardation of rusting in the winter months and speeding-up in the summer.

When the test was terminated after 503 weeks, the two specimens annealed at 650° C. for 30 min. had not failed, although the even black appearance was breaking up and failure would probably not have been long delayed. Figure 4 shows the appearance of the pairs of as-received wires, and wires annealed for 30 min. at 550° C. and at 650° C. after 503 weeks' exposure; uncorroded wires are included for comparison.

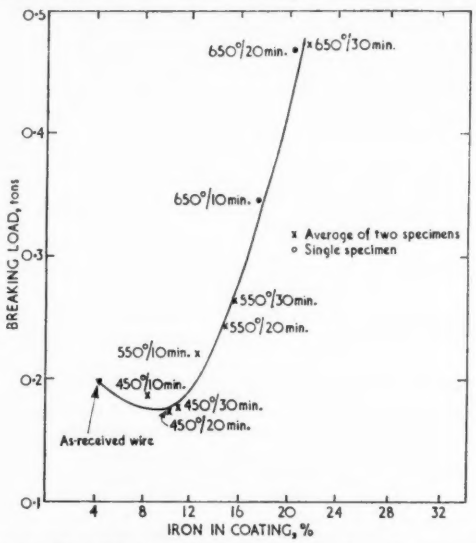


Fig. 6—Breaking load of as-received and annealed galvanized wires after exposure for 503 weeks

Mechanical Strength of Wires after Test

At the end of the 503 weeks' test the breaking load of some of the wires was determined and the results are shown in Fig. 6. The breaking load of the as-received wires had been reduced from 0·850 to

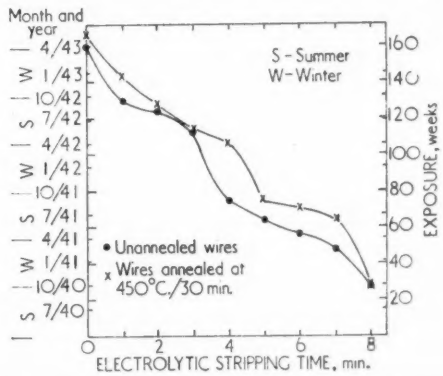


Fig. 7—Time for first appearance of red rust on annealed and unannealed galvanized wires after various degrees of electrolytic stripping

0·198 ton. All wires containing 12% or more of iron in the coating had a greater residual strength. The wires annealed at 650° C. for 30 min. lost no strength at all.

Relative Resistance to Corrosion of Successive Layers of Coatings As-Received and Annealed at 450° C./30 min.

As-received coatings annealed at 450° C. for 30 min. were stripped electrolytically to remove successively greater amounts of coating, and then exposed to the atmosphere. Two factors may influence the interpretation of the results (Fig. 7) :

(i) Variation in the properties of the various layers of the coating, and
(ii) Variation in the severity of the corrosion conditions.

Both curves change in similar ways as the seasons change, although at any one time layers of different compositions are exposed. The form of the curves suggests that the rate of corrosion for both as-received and annealed coatings was about the same during any given season, irrespective of the nature of the layer exposed. The indications from these results are therefore :

(i) The rate of corrosion of the outer zinc layer in an as-received coating was similar to that of the alloy layers, and
(ii) The corrosion rate was higher in summer (April–September) than in winter (October–March).

The latter result supports the conclusion previously reached from consideration of Fig. 5.

This seasonal variation is presumably due to the combined effects of a number of climatic factors, amongst which the presence of moisture and the temperature may be the most important. Schikorr,[7] in work on the atmospheric corrosion of solid zinc at Berlin, found that corrosion as measured by loss of weight was greater in the winter than in the summer and closely followed the changes in the amount of sulphurous gases in the atmosphere.

EXPOSURE OF ANNEALED WIRES WITH DAMAGED COATINGS

Annealed wires (MHZ) were prepared by the methods already described and the coatings were then damaged by either :

(i) Winding the wires round steel formers, or
(ii) Making deep notches with a triangular file, and by filing with a flat file for ⅜-in. lengths to a level well below the coating, thus exposing bare steel.

Table V

LIFE OF GALVANIZED WIRES WOUND ROUND STEEL FORMERS AFTER VARIOUS ANNEALING TREATMENTS, WEEKS

Dia. of Former, in.	Annealing Treatment			
	None	450° C. 30 min.	550° C./30 min.	650° C./30 min.
0·118	133	*	*	*
0·236	170	133	300	>389†
0·491	*	170	257	389

* Not tested † Not yet failed

The damaged wires were exposed on the same stand as the main set of wires, but facing north-east instead of south-west, on 27th November, 1944.

The results for wires wound round formers are given in Table V, the figures referring to single specimens.

In spite of the crumbling of the coating in the spirals, it is clear that annealed wires have a much greater life than unannealed wires.

The results for the filed wires are given in Table VI. During the first few weeks the parts so exposed on the annealed wires were covered with a thin layer of rust, but not rough red rust such as that taken to indicate failure. Afterwards, the bared parts became coated with a layer of corrosion product similar to that on the undamaged part of the wire, consisting of a thick layer of orange-red rust covered with the black layer. They could in fact only be detected with difficulty. After 233 weeks, more than a year after the failure of the wires annealed at 450° C./30 min. and 500° C./30 min., the original bared patches were the only parts of these wires which showed the black layer. They were cleaned in inhibited sulphuric acid and the parts originally bared were, if anything, less pitted than the rest of the specimens. The same was true of the filed patches on the wires annealed at 600° C. which failed at 300–340 weeks. The wire annealed at 650° C. had not failed after 389 weeks and is still exposed, the bared parts being covered with the black layer.

EXPOSURE OF AS-RECEIVED AND ANNEALED GALVANIZED STEEL SHEETS

Nine 3 in. × 4 in. sheet specimens (Mark JQX, *see* Table I) were exposed, six of them after annealing at 550° C. for 45 min. Three of the six annealed specimens were exposed without the subsequent acid dip to remove annealing scale. The average percentage of iron in the annealed coatings was 17·5. The specimens were exposed 9 in. above and at 30° to the roof, facing south-west, on 20th May, 1943. The objects were to confirm that the beneficial effects of annealing applied to sheets as well as wires, and also to make possible a more detailed examination of the layer of corrosion product than was possible with the wires.

The results in Table VII, which refer to the upper surfaces of the sheets, show that the increased life due to annealing was considerable, and close to that of wires which received annealing treatments giving about the same average iron content in the coating (*see* Table IV). Some added protection appeared to be given by the annealing scale.

COMPOSITION AND THICKNESS OF THE LAYER OF CORROSION PRODUCT

On examining annealed specimens in the black stage, a thick layer of yellow-orange rust was found

Table VI

LIFE OF GALVANIZED WIRES CONTAINING NOTCHES AND PATCHES OF BARED STEEL

Annealing Treatment	Life, weeks
As-received	127, 133
450° C./30 min.	165
500° C./30 ,,	170
600° C./30 ,,	300, 340
650° C./30 ,,	>389*

* Specimen not yet failed

Table VII

LIFE UNDER URBAN ATMOSPHERIC CONDITIONS OF ANNEALED GALVANIZED STEEL SHEETS (JQX SHEET)

Annealing Treatment	Life, weeks	Average Life, weeks
None	164, 173, 173	170
550° C./45 min.	274, 278, 351	301
550° C./45 min. (scale not removed)	303, 338, 343	328

underneath the black film. Near the metal it was hard and compact.

When the removed corrosion product was cleaned of tarry matter by washing with benzene and then treated with dilute hydrochloric acid (33%), a small black residue remained which was magnetic and insoluble in concentrated acids or warm *aqua regia*. This probably formed the original black surface layer. It did not appear to be a sulphide. X-ray examination showed the presence in it of silica (α quartz form) and α-Fe_2O_3 (hematite), and there was also an indication of the presence of one or more of the spinel structures Fe_3O_4, Fe_2O_3.ZnO, and γ-Fe_2O_3. The corrosion product as a whole also contained sulphide and zinc oxide, the sulphide forming a layer between the residual coating and the orange-red rust.

The thickness of the layer of corrosion product on annealed and unannealed specimens was compared by measurements carried out on hot-dipped galvanized sheet PAL (Table I). Some 4 in. × 1½ in. sheets were annealed at 550° C. for 45 min., and exposed with unannealed sheets. After six years' exposure, and before any of the specimens had failed, the average thickness of the corrosion product was 0·0032 in. on the annealed, and 0·0013 in. on the unannealed sheets.

SUGGESTED REASONS FOR THE INCREASED PROTECTION AFFORDED BY ANNEALING

The life of the annealed wires increased with the average iron content of the coating when this exceeded about 10%. Increasing amounts of the zinc-rich Γ' phase will probably be present as the iron content increases, until at the highest iron content (21·6%), which gives the longest life, the coating probably consists largely of this phase. The corrosion products formed by this phase may give more protection against corrosion than those formed by coatings containing less iron.

The black layer does not completely cover the coating unless the latter is rich in iron, and hence the presence of the Γ' phase may be necessary for its formation. It is insoluble and adherent, and may act as a partially waterproof covering which reduces the amount of rain which soaks through to the coating, thus reducing corrosion and preventing the dissipation by rain of the protective corrosion products lying between it and the coating.

Bare steel patches may be protected by the action of corrosion products from the adjacent coating and by the formation of the black layer.

It is improbable that the increased protection is due to any material deposited as particles from the atmosphere. The fact that the coating life is a function of the iron content of the coating before exposure (Table IV) is strong evidence that the protective material is either some substance existing in the original coating or corrosion product, or is produced by a reaction between the coating or the corrosion product and the components of the atmosphere.

CONCLUSIONS

For the particular conditions of exposure to the London atmosphere described, the following conclusions may be drawn :

(1) The life of hot-dipped galvanized wire or sheet can be substantially increased by a suitable annealing treatment. The longest life obtained, that with a coating containing 21·6% of iron, was more than three times the life of an unannealed coating.

(2) Annealing hot-dipped galvanized wires reduces the resistance of the coating to deformation, but even severely damaged annealed coatings last much longer than undamaged as-received coatings.

(3) For ordinary hot-dipped galvanized steel wire the rates of corrosion of the outer zinc and alloy layers appear to be approximately the same.

(4) It is probable that the rate of atmospheric corrosion of galvanized coatings, whether annealed or not, varies with the seasons, being, in the present tests, greater in the summer and autumn than in the winter and spring.

(5) The reason why annealed coatings confer longer protection on the basis steel is undoubtedly connected with the character of the corrosion product. The rate of corrosion may be reduced because a thin black layer of an insoluble compound on the surface of the corrosion products acts as a partially waterproof covering, thus preventing rain from soaking through to the coating and preserving the protective corrosion products, thereby lengthening the period during which they retard corrosion.

Acknowledgments

The author desires to thank the Director and Council of the British Non-Ferrous Metals Research Association for permission to publish the results of this work, and also to thank his colleagues for helpful discussions.

References

1. J. C. HUDSON and T. A. BANFIELD : *J. Iron Steel Inst.*, 1946, No. II, pp. 229–264.
2. O. W. STOREY : *Metallurgical and Chemical Engineering*, 1916, vol. 14, pp. 683–691.
3. J. L. SCHUELER : *Transactions of the American Electrochemical Society*, 1925, vol. 47, pp. 201–226.
4. S. C. BRITTON : *J. Inst. Metals*, 1936, vol. 58, pp. 211–225.
5. J. SCHRAMM : *Z. Metallkunde*, 1936, vol. 28, pp. 203–207.
6. J. SCHRAMM : *Ibid.*, 1937, vol. 29, pp. 222–224.
7. G. SCHIKORR and I. SCHIKORR : *Ibid.*, 1943, vol. 35, pp. 175–181.

ANDREW CARNEGIE SCHOLARSHIP REPORT

The Effect of Sodium Oxide Additions to Steelmaking Slags

Part II—DEPHOSPHORIZATION OF STEEL BY SODA-SLAGS

By W. R. Maddocks, Ph.D., and E. T. Turkdogan, Ph.D., M.Met.

SYNOPSIS

In a previous paper the effect of soda-slags under steelmaking conditions on the removal of phosphorus at low temperatures was studied. Further experimental melts have now been made at 1400° and 1550° C., and the results have been considered in relation to the earlier data. It is shown that the effect of temperature on dephosphorization is not so great as was first anticipated. The soda/silica and iron/silica ratios are the main factors determining the extent of the removal of phosphorus from iron. It has been shown that the composition of the slag should be kept within such limits that the slag will be oxidizing, and that there will be sufficient sodium oxide to combine with the phosphorus pentoxide in the slag. Some interesting relationships have been shown to exist between the slag composition and its density.

EXPERIMENTAL WORK

DETAILS of the experimental procedure were given in Part I,[1] and there have been no changes in the melting technique. In most cases, no difficulty has been experienced in controlling the temperature, which could be kept within the limits of ± 10° C. at 1400° and 1550° C. for about 20–30 min.

Some modifications were made in the choice of the hearth refractories. In most of the melts silica flour was used, but in these hearths the silica content of the slag could not be retained below 40% at 1550° C., although this limit could be lowered to 30% at 1400° C. The increase in the corrosive effect of the soda-slags on the hearths with rising temperature was to be expected, and so the predetermined range of silica concentration in the slag was taken into account when choosing the hearth material. For slags whose final silica content had to be less than 30%, the hearths were made of 250-mesh electrically fused pure magnesia, and above that range of acidity pure silica flour was used. With both these refractory materials, however, there was always some mechanical erosion on the hearth during the experiment, and consequently the slag was contaminated with the hearth material. It should not be assumed that the above observations are a measure of the corrosive effect of soda-slags on the refractory linings of the furnace, because in these experimental melts the hearths were in a green state, whereas in practice the surface of the hearth is always glazed. An attempt was made to glaze the surface of the silica hearths, but this was a long process and offered little advantage. Some melts were made on alumina and ganister hearths. The former did not appear to be a good material for the purpose, but ganister hearths were somewhat better than silica flour hearths because they set quite hard after drying in air for about a day. The slags, however, contained rather high proportions of alumina (up to 9·0%), because the ganister was already mixed with bond-clay. To improve the mechanical strength of the hearths, different types of bond were tried, *e.g.*, water, water-glass, sulphite-lye, and bond-clay. Water-glass was found to be quite satisfactory.

The synthetic slags, *i.e.*, first slag and soda-oxidizer, were prepared as described in Part I.[1] The composition was within the following ranges :

	SiO_2, %	Fe_2O_3, %	MnO, %	CaO, %
First slag	40–60	20–30	15–25	3–5
	SiO_2, %	Fe_2O_3, %	Na_2O, %	
Soda-oxidizer	0–50	0–50	30–60	

The amounts of the first slag and soda-oxidizer were adjusted according to the required slag composition, so that the total slag additions weighed 200 g.

Two types of pig iron were used with the following compositions :

	P, %	C, %	Mn, %	Si, %	S, %
A	1·34	2·94	0·32	0·14	0·08
B	0·52	1·06	0·62	0·63	0·11

In melt *SH*11 the charge contained 0·14% of P, and in melts *SH*12 and *NS*2 1·60% of P.

The experimental melts are grouped into series depending on the refractory material of the hearth, the original phosphorus content of the charge, and the temperature (*see* Table I). No soda-oxidizer additions were made to the melts in series *NS*.

Silica thermocouple sheaths were chosen for siliceous hearths, and alumina sheaths for magnesia hearths. The alumina sheaths, however, were preferred in all the melts at 1550° C.

The chemical analyses of the metal and slag samples, given in Table II, were made by standard methods. The sodium oxide percentages were determined satisfactorily by difference.

STABILITY OF Na_3PO_4 AND LOSS OF Na_2O

Oelsen and Wiemer[2] studied the immiscibility

A report, received 14th July, 1951, on research carried out with the aid of a grant from the Andrew Carnegie Research Fund.

Dr. Maddocks is Senior Lecturer in Ferrous Metallurgy, University of Sheffield, and Dr. Turkdogan is in the Chemistry Department of the British Iron and Steel Research Association.

Table I

DETAILS OF THE EXPERIMENTAL MELTS

Series	Hearth Material	Bond	Charge, % P	Temperature, ° C. (± 10° C.)
SA (1 to 15)	Silica flour	Sulphite-lye	1·34	1400
GA (1 to 2)	Ganister	Bond-clay	1·34	1400
MA (1 to 4)	Magnesia	Sulphite-lye	1·34	1400
***NS*1**	Silica flour	Sulphite-lye	1·34	1400
SH (1 to 10)	Silica flour	Water	0·52	1550
GH (1 to 6)	Ganister	Bond-clay	0·52	1550
AH (1 to 2)	Alumina	Water	0·52	1550
PGH (1 to 3)	Ganister	Bond-clay	1·34	1550
PMH (1 to 5)	Magnesia	Water-glass	1·34	1550
MH (1 to 4)	Magnesia	Water-glass	0·52	1550
***SH*11**	Silica flour	Water-glass	0·14	1550
***SH*12**	Silica flour	Water-glass	1·60	1550
***NS*2**	Silica flour	Water-glass	1·60	1550
NS (3 to 5)	Silica flour	Water	0·52	1550

phenomena in ferrous oxide/sodium phosphate slags. The immiscibility gap in the Na_2O–P_2O_5–FeO ternary system closely resembled that in the CaO–P_2O_5–FeO ternary system previously investigated by Oelsen and Maetz.[3] The comparison of these two ternary systems revealed the greater stability of sodium ortho-phosphate with respect to calcium ortho-phosphate. Oelsen and Wiemer made a more direct approach by investigating the effect of sodium oxide additions to the calcium ortho-phosphate/wüstite melts. It was found that considerably more calcium oxide than sodium oxide was forced into the wüstite layer in the melts containing CaO, Na_2O, FeO, and P_2O_5. Moreover, the calcium content of the wüstite layer corresponded very closely to the figure calculated on the assumption that all the CaO was expelled from the phosphate layer into the wüstite layer by the added Na_2O. Thus,

$$\underset{\text{(top layer)}}{Ca_3P_2O_8} + 3Na_2O \rightleftharpoons \underset{\text{(top layer)}}{2Na_3PO_4} + \underset{\text{(bottom layer)}}{3CaO} \quad \ldots\ldots(1)$$

The behaviour of sodium ortho-phosphate in lime-bearing slags has already been studied.[1] The synthetic slags contained certain proportions of sodium ortho-phosphate, calcium oxide, iron oxide, and silica; after the melt the amounts of sodium oxide and phosphorus pentoxide approached the composition of the sodium ortho-phosphate originally added to the slags. It was thus concluded that calcium could not replace sodium in the ortho-phosphate, otherwise the liberated sodium oxide would have been lost. This indicated the stability of sodium ortho-phosphate compared with calcium ortho-phosphate.

The evidence, from these two independent sources, fully supports the theory that the reaction represented by equation (1) proceeds from left to right. The heat of reaction is — 87·75 kg.cal./mole. Additional support may be obtained by comparing basic conditions in soda-slags with those in lime-slags for varying degrees of dephosphorization. For example, in lime-slags the concentration of lime must be above 30–32% for a reduction in phosphorus, whilst under soda-slags containing about 60% SiO_2, 7% Na_2O, 10% FeO, the remainder being lime, magnesia, and alumina, a 15–20% reduction in phosphorus is possible. Moreover, a basicity ratio of about 1·5–2·0 gives a phosphorus distribution factor of almost zero in lime-slags, whereas under soda-slags the phosphorus distribution factor increases from 100 to 200 for the same range of basicity ratio.

In Part I the loss of sodium oxide taking place in the pre-fusion of the slags and during the melt was considered. During the sintering of the synthetic slags there was some loss of soda, which increased as the total acidity of the mixture decreased; but during the melt, however, the loss was greater. It was found that this loss could be reduced to a small amount by adjusting the lime/silica ratio. More recent data allow the explanation of this loss to be modified.

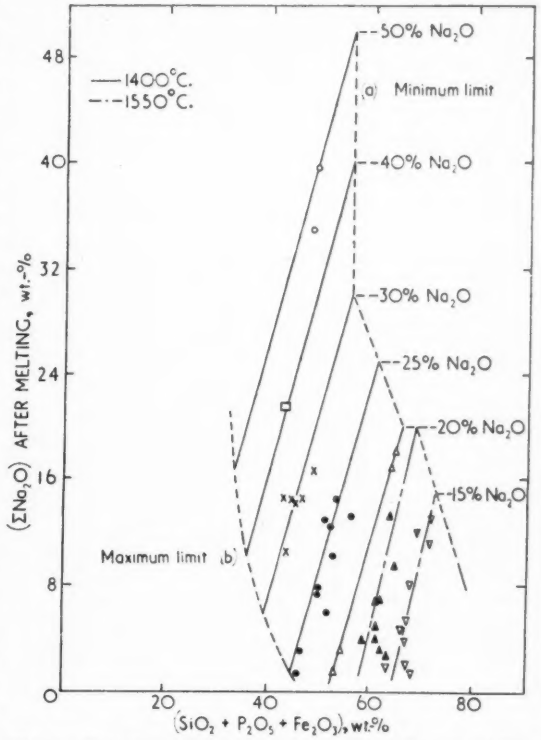


Fig. 1—Relationship between loss of Na_2O and acidity of slag

When molten iron is poured on sodium carbonate, excessive sodium fume is evolved. Yet, when molten iron is poured into a molten synthetic slag containing soda, silica, and iron oxides, there is very little, if any, soda fume. That iron can reduce sodium oxide at elevated temperatures has been confirmed by Carter,[4] who suggested that the reaction resulted in the formation of ferrous oxide and sodium vapour, *i.e.*,

$$Na_2O + Fe \rightleftharpoons FeO + 2Na \quad \ldots\ldots\ldots\ldots\ldots (2)$$

He found that the reduction of sodium oxide increased with temperature.

Table II
CHEMICAL ANALYSES OF SLAGS AND METALS

Melt No.	Slag Analysis, wt.-%										Metal Analysis, wt.-%		
	ΣFe	FeO	Fe_2O_3	SiO_2	P_2O_5	S	Na_2O	CaO	MnO	MgO	Al_2O_3	P	S	C
*SA*1	23·32	26·10	4·33	33·96	5·38	0·150	10·58	7·12	6·22	2·46	3·70	0·17	0·100	1·50
*SA*2	19·78	22·22	3·58	34·30	5·58	0·098	14·73	6·54	7·44	2·55	2·96	0·25	0·085	1·72
*SA*3	19·22	22·12	2·89	37·60	4·60	0·098	14·37	6·52	7·68	1·35	2·77	0·52	0·061	1·95
*SA*4	21·04	24·50	2·86	37·68	3·98	0·098	14·43	4·74	7·80	1·20	2·71	0·56	0·055	1·95
*SA*5	20·56	21·66	5·32	40·42	4·17	...	7·93	8·80	8·70	2·10	0·90	0·78	...	1·21
*SA*6	25·30	29·25	3·66	40·70	2·30	...	3·08	10·80	7·08	2·11	1·20	0·64	...	1·46
*SA*7	15·54	17·88	2·35	43·16	3·08	0·071	16·82	4·30	8·54	2·50	1·30	0·70	0·101	1·88
*SA*8	19·56	22·55	2·88	46·62	1·67	0·034	13·12	4·88	6·26	1·01	0·98	0·84	0·072	1·64
*SA*9	17·76	20·26	2·86	47·58	1·81	0·055	12·66	6·00	6·97	1·08	0·73	0·83	0·060	1·77
*SA*10	18·04	21·10	2·33	48·77	1·68	0·024	10·29	6·68	7·25	1·01	0·87	0·93	0·100	1·57
*SA*11	16·78	20·27	1·46	50·54	0·92	0·050	14·50	5·04	5·90	0·40	0·92	1·05	0·100	2·20
*SA*12	7·08	7·56	1·72	57·94	1·51	0·050	13·30	4·00	12·42	0·81	0·69	1·03	0·065	2·01
*SA*13	5·60	5·53	1·86	59·60	1·98	0·050	17·07	3·70	9·04	0·55	0·62	1·16	0·069	2·33
*SA*14	4·57	4·16	1·90	59·66	2·21	0·050	18·25	3·74	9·08	0·48	0·47	1·04	0·048	2·27
*SA*15	26·58	28·90	3·32	45·26	1·17	0·156	7·28	4·92	4·74	2·28	1·97	0·76	0·052	0·66
*GA*1	24·46	27·00	4·95	47·00	1·24	0·155	1·55	3·38	5·73	1·00	8·00	0·85	0·036	1·54
*GA*2	18·40	19·00	5·18	48·96	1·88	0·145	13·28	5·62	0·18	1·77	3·98	0·88	0·059	1·66
*MA*1	3·30	2·88	1·83	43·20	3·37	0·173	39·62	1·93	0·55	4·95	1·50	0·95	0·022	2·33
*MA*2	6·20	6·17	2·01	42·56	3·61	0·208	35·02	2·13	0·63	6·16	1·50	0·96	0·050	2·29
*MA*3	8·54	6·95	4·49	28·24	10·37	0·224	21·63	5·56	10·24	10·05	1·80	0·21	0·066	1·44
*MA*4	20·88	11·63	16·88	24·93	4·98	0·232	14·41	7·20	6·92	10·23	2·59	0·028	0·029	0·43
*NS*1	23·80	29·65	1·03	35·40	0·40	...	0·00	13·00	18·11	3·05	0·30	1·27	...	1·03
*SH*1	6·15	5·92	2·22	65·51	0·15	0·104	8·05	8·30	7·58	0·94	1·22	0·45	0·085	0·13
*SH*2	5·60	5·40	2·00	63·08	0·14	0·075	9·62	7·90	9·28	0·96	1·54	0·45	0·093	0·33
*SH*3	5·35	4·92	2·07	66·24	0·19	0·092	11·96	7·00	4·98	1·21	1·34	0·45	0·072	0·22
*SH*4	5·25	4·83	1·78	69·90	0·15	0·118	12·71	7·00	1·76	0·75	1·00	0·45	0·076	0·39
*SH*5	6·00	6·05	1·81	70·00	0·23	0·102	11·22	7·20	1·76	0·68	0·95	0·48	0·078	0·16
*SH*6	19·39	20·52	4·92	61·90	0·30	0·103	3·84	5·24	1·46	0·72	1·00	0·39	0·044	0·03
*SH*7	16·15	18·29	2·76	62·96	0·32	0·115	4·48	7·24	1·76	1·02	1·05	0·42	0·075	0·06
*SH*8	15·17	17·43	2·30	64·60	0·35	0·118	5·21	5·69	1·70	1·00	1·60	0·37	0·061	0·10
*SH*9	19·30	22·74	2·29	60·52	0·20	0·110	2·82	6·50	1·58	1·60	1·64	0·49	0·110	0·06
*SH*10	10·06	9·62	3·69	64·86	0·29	0·055	1·23	11·16	3·68	3·83	1·58	0·40	0·063	...
*SH*11	27·07	31·61	3·58	48·00	0·26	0·190	5·87	2·92	3·66	2·34	1·67	0·100	0·037	...
*SH*12	27·97	34·32	1·83	52·00	0·77	0·090	3·27	2·08	2·92	1·05	1·67	1·13	0·043	...
*GH*1	31·30	35·22	5·59	40·00	0·49	0·090	2·37	4·60	2·72	2·60	6·32	0·19	0·042	...
*GH*2	15·56	15·23	5·32	50·80	0·42	0·063	3·55	12·84	4·06	2·17	5·55	0·32	0·060	...
*GH*3	12·55	12·86	3·65	58·13	0·30	0·047	6·93	4·84	4·22	2·32	6·70	0·34	0·084	...
*GH*4	13·35	13·70	3·86	56·81	0·42	0·156	5·18	4·32	2·85	3·00	9·70	0·24	0·081	...
*GH*5	16·01	18·39	2·45	59·61	0·44	0·127	3·05	4·84	3·12	2·21	5·76	0·30	0·106	...
*GH*6	16·30	18·90	2·23	58·61	0·41	0·133	4·00	5·52	2·83	2·04	5·33	0·37	0·108	...
*AH*1	22·50	21·50	8·22	20·00	0·51	0·134	1·16	9·23	4·63	3·22	31·60	0·19	0·089	...
*AH*2	13·66	13·86	5·12	24·38	0·40	0·041	6·54	6·18	6·49	2·44	34·55	0·21	0·063	...
*PGH*1	16·38	17·36	4·13	56·70	0·61	0·153	7·07	4·00	0·19	1·69	8·10	0·79	0·059	1·60
*PGH*2	19·28	22·50	2·28	54·60	0·52	0·175	2·28	3·45	4·20	1·00	9·00	1·00	0·122	0·44
*PGH*3	20·10	23·28	2·86	51·89	0·34	0·163	1·82	5·20	5·00	1·20	8·25	0·87	0·064	0·88
*PMH*1	24·42	26·44	5·52	23·30	4·65	...	6·11	13·72	12·00	7·46	0·80	0·04	...	0·16
*PMH*2	53·44	60·00	9·71	6·24	2·55	...	3·12	6·32	3·60	7·56	0·90	0·15	...	0·05
*PMH*3	44·36	40·55	18·36	9·08	1·33	0·301	2·87	7·92	5·08	10·47	4·04	0·030	0·042	...
*PMH*4	40·88	38·68	15·44	12·00	2·51	0·207	3·52	7·20	5·04	10·50	4·90	0·021	0·038	0·05
*PMH*5	35·20	31·76	16·46	16·64	3·41	0·195	5·07	7·76	5·14	10·39	3·00	0·013	0·031	...
*MH*1	42·82	37·36	19·71	14·12	3·32	0·210	5·26	4·44	4·70	6·46	4·42	0·013	0·025	...
*MH*2	38·42	41·44	8·87	15·82	3·74	0·210	5·20	7·32	1·56	11·67	4·00	0·023	0·042	...
*MH*3	34·26	33·32	11·96	22·18	3·06	0·167	3·98	4·00	5·84	10·14	5·35	0·042	0·057	...
*MH*4	26·28	22·45	12·62	28·22	3·42	0·172	6·46	3·60	7·12	11·76	4·18	0·024	0·049	...
*NS*2	32·12	39·12	2·43	47·00	0·10	0·120	0·00	6·56	2·87	1·00	2·62	1·67	0·030	...
*NS*3	13·59	15·79	1·87	60·09	0·08	...	0·00	7·10	13·45	0·86	0·97	0·61	...	...
*NS*4	12·34	14·11	1·94	61·90	0·08	...	0·00	8·40	13·27	0·56	0·62	0·59	...	...
*NS*5	13·28	15·48	1·77	60·17	0·17	...	0·00	7·34	11·93	3·80	0·45	0·63	...	...

In siliceous slags, however, Na_2O will most probably be bound to phosphoric acid, silica, and ferric oxide. In Fig. 1 the soda content of the slag has been correlated with its acidity by plotting the percentage of sodium oxide against the sum of the percentages of phosphorus pentoxide, silica, and ferric oxide in the slag. A family of lines is drawn through the experimental points for varying original sodium oxide contents of the added synthetic slags, and for different temperatures, *i.e.*, 1400° and 1550° C. Considering the variation in slag bulk, the scatter of the points is not very great. A decrease in the acidity of the slag results in appreciable loss of sodium oxide ; the relationship is linear for a given initial percentage of soda in the synthetic slag. Extrapolation of the lines to the original soda percentages gives the acidity figures when there is no loss of soda. The locus of these points, *i.e.*, curve *a*, indicates the contents of acid oxides at which no loss of soda would occur. Since sodium phosphate appears to be a relatively stable compound, and, further, since in slags containing less than 30% of silica all the sodium oxide is combined with phosphoric acid (*see* p. 133), the minimum values to which the soda contents are likely to be reduced are indicated by the dotted curve *b*.

Temperature has a very pronounced effect on the relationships shown in Fig. 1. A slag containing 65% of acids and initially 20% of soda will lose only 5% of its soda at 1400° C., whereas a similar slag at 1550° C. will lose 35% of its soda. The slope of the lines increases with temperature.

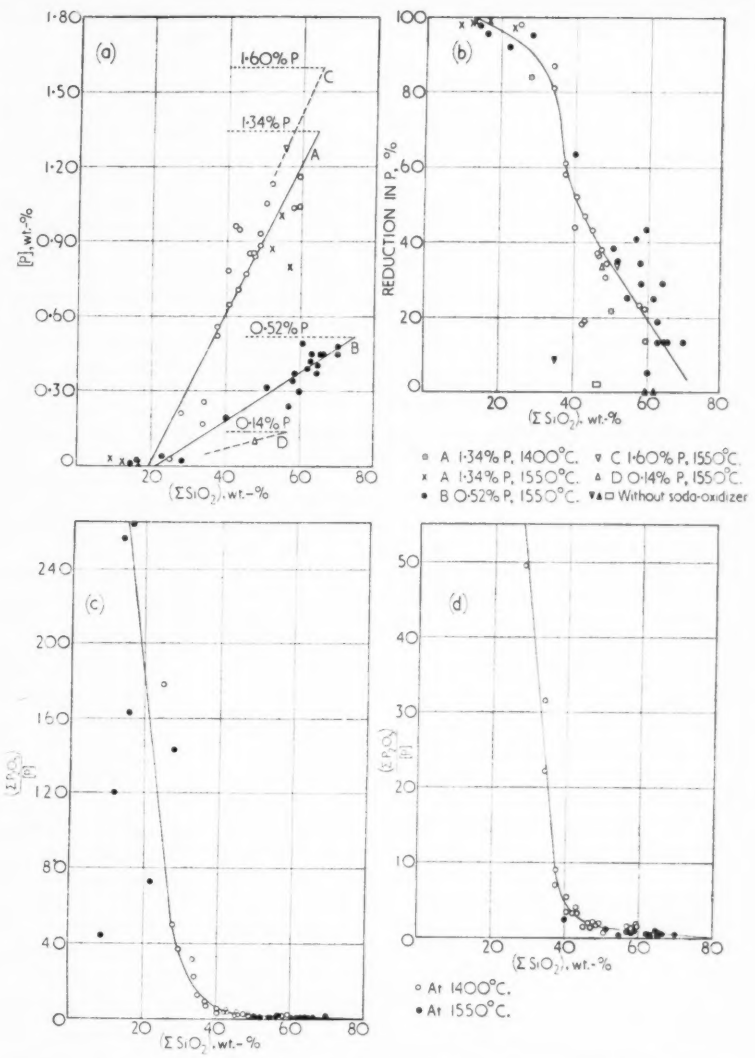


Fig. 2—Effect of silica concentration on : (*a*) and (*b*) the removal of phosphorus ; (*c*) and (*d*) the phosphorus distribution factor

DEPHOSPHORIZING REACTIONS

Figure 2*a* shows that any given percentage of total silica in the slag is in equilibrium with the percentage of phosphorus in the metal. This percentage increases with the initial phosphorus content of the charge because the varying amount of phosphorus removed from the metal results in the formation of differing amounts of phosphorus pentoxide. For the same reason, for a given percentage of phosphorus in the refined metal, the total silica content of the slag increases as the percentage of the original phosphorus in the charge decreases. Therefore, in adjusting the total silica content of a slag to refine iron to a predetermined percentage of phosphorus, the original phosphorus in the metal must be taken into account. For every initial phosphorus content in iron there is a limiting silica concentration in the slag, beyond which no reduction in phosphorus can be expected.

The above relationship may be shown in a more comprehensive way by combining the percentages of initial and final phosphorus in terms of the percentage reduction in phosphorus (*see* Fig. 2*b*). The percentage reduction in phosphorus under the slags of melts conducted in the absence of a soda-oxidizer is exceedingly low compared with other melts of the same silica content.

In Fig. 2*c* the phosphorus distribution factor, *i.e.*, $(\Sigma P_2O_5)/[P]$, is plotted against the percentage of total

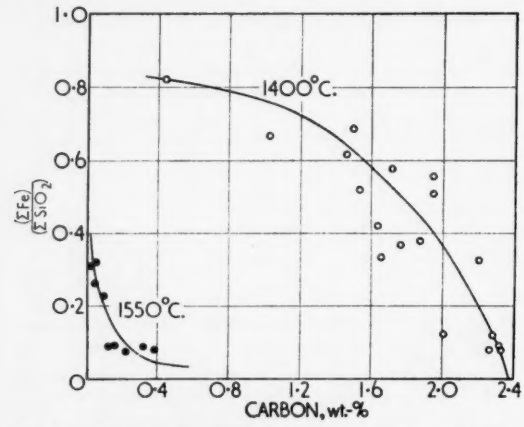


Fig. 3—Effect of iron/silica ratio and temperature on the carbon content of the metal

silica in the slag, and is shown to increase as the total silica decreases. Below a total silica content of 30% the curve may be a straight line, but, unfortunately, the experimental points are widely scattered. The scatter is attributed to the excessive slag absorption by the magnesia hearths at 1550° C. and the consequent fluctuation of the slag bulk. To obtain a better picture of the distribution of the points when the slag contains more than 30% total silica, part of Fig. 2*c* has been reproduced on a larger scale in Fig. 2*d*. As the total silica falls from 40 to 30%, there is a rapid rise in the phosphorus distribution factor from 5 to 50. When the total silica increases from 40 to 70%, the distribution factor falls from 5 to 1.

It is considered that the curves in Figs. 2*a* and *d* are significant when soda-slags are to be applied in practice. Although the presence of silica is necessary to retain sodium oxide in the slag, its high concentration retards and/or reverses the reaction of dephosphorization. The total silica concentration in the slag indirectly controls the dephosphorizing reaction by its influence on the oxidizing power of the slag, and directly controls the elimination of phosphorus by limiting the amount of sodium oxide available for combination with phosphorus pentoxide. To overcome the effects of high silica it is therefore essential to increase the percentages of soda and iron oxide in soda-slags.

In Fig. 3 the $(\Sigma Fe)/(\Sigma SiO_2)$ ratio is plotted against the percentage of carbon in the refined metal. The scatter results from the undue variation in the amount of carbon lost during melting. At both 1400° and 1550° C., the reduction in carbon increases with the iron/silica ratio and, for a given iron/silica ratio, the reduction in carbon increases very considerably as the temperature rises from 1400° to 1550° C. The iron/silica ratio is therefore an indication of the oxidizing power of the slag.

Figure 4*a* shows the effect of the iron/silica ratio on the extent of dephosphorization. The scatter of the points is attributed to the varying percentages of sodium oxide. For a 0·50 change in the abscissa the variation in the ordinate is about 20%, and for a fixed iron/silica ratio the points travel into the higher phosphorus reduction area as the soda/silica ratio increases. This is illustrated more clearly in Fig. 4*b*, in which the percentage reduction in phosphorus is plotted against the product of these two ratios, *i.e.*, $[(\Sigma Fe)(\Sigma Na_2O)]/(\Sigma SiO_2)^2$. When this ratio is below 0·23, the relationship is linear, and the line passes through the origin of the co-ordinates. Between 0·23 and 0·33, there is a sharp change in the slope of the curve, and above 0·33 the curve becomes asymptotic to the horizontal line signifying a 100% reduction in phosphorus. For a 60 to 80% reduction in phosphorus, the required value for the $[(\Sigma Fe)(\Sigma Na_2O)]/(\Sigma SiO_2)^2$ ratio is from 0·15 to 0·23.

The principal relationship between the slag components which are active in the dephosphorizing reaction may be seen in Fig. 5*a*, in which the soda/silica ratio is plotted against the percentage of phosphorus pentoxide in the slag. The scatter in the experimental points may be eliminated by taking into account the variations in the slag components. Figure 5*a* shows that the field can be divided into sections corresponding to different ranges of silica content as follows :

Section I —Below 30% SiO_2
Section II —Between 30 and 40% SiO_2
Section III—Between 40 and 55% SiO_2
Section IV —Above 55% SiO_2

The curves drawn through the experimental points in the same range of total iron have the shape of a

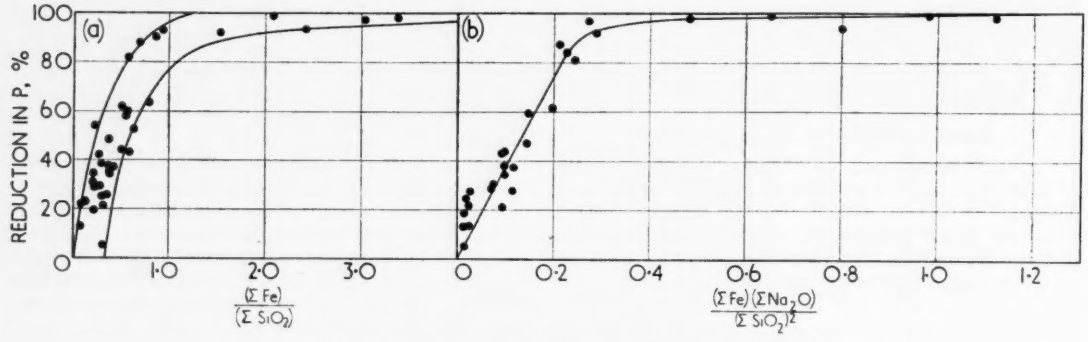
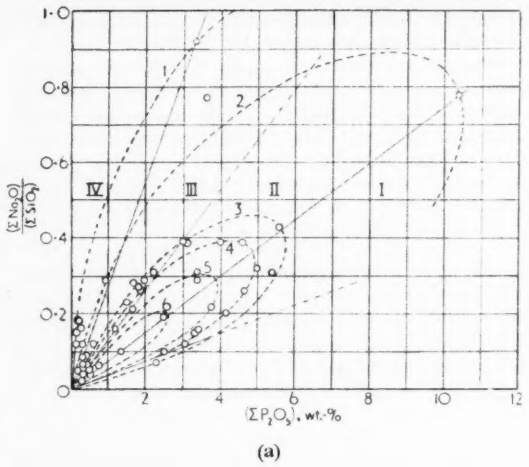


Fig. 4—Percentage reduction in phosphorus plotted against:

(*a*) $\frac{\Sigma Fe}{\Sigma SiO_2}$; (*b*) $\frac{(\Sigma Fe)(\Sigma Na_2O)}{(\Sigma SiO_2)^2}$



(a)

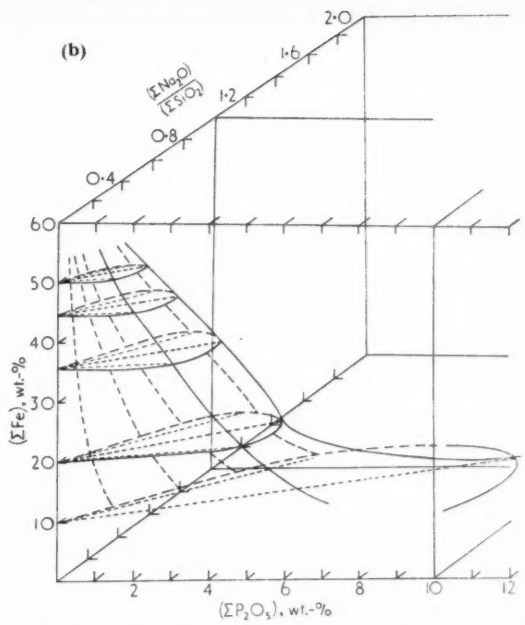


Fig. 5—Relationship between ΣP_2O_5 and soda/silica ratio shown on: (*a*) A two-dimensional figure; (*b*) a three-dimensional figure

semi-lemniscate with a common point resting at the origin of the co-ordinates. These are referred to as 'iron-curves,' and represent the following ranges :

Iron-curve 1—Between 3 and 5% ΣFe
Iron-curve 2—Between 5 and 15% ΣFe
Iron-curve 3—Between 15 and 25% ΣFe
Iron-curve 4—Between 25 and 35% ΣFe
Iron-curve 5—Between 35 and 45% ΣFe
Iron-curve 6—Between 45 and 55% ΣFe

The slight scatter of the points within the silica sections and iron-curves may be attributed to the variation of temperature and to other slag components, and therefore the following conclusions may be drawn from the characteristics shown in Fig. 5*a* :

(1) In a given silica section, the phosphoric acid contents of the slags increase with the soda/silica ratio
(2) To attain a given phosphorus pentoxide in the slag, the soda/silica ratio should be increased as the total silica concentration in the slag increases
(3) For a given soda/silica ratio, the total silica content of the slag must be reduced if the slag is to absorb higher percentages of phosphoric acid
(4) Along an iso-silica line, *e.g.*, a boundary between the silica sections, the total iron content of the slag decreases as the values of the co-ordinates increase
(5) For a given iron-curve, the percentage of phosphoric acid in the slag is determined, firstly, by the silica concentration, and secondly, by the sodium oxide concentration. The iron-curve becomes larger as the total iron decreases because, under these conditions, the effects of silica and soda/silica ratio are more prominent
(6) The iron-curves appear to be symmetrical about an iso-silica line, which could be 35% SiO_2.

The variation in the slag components, which are directly connected with the dephosphorizing reactions, may be co-ordinated in a three-dimensional figure (*see* Fig. 5*b*). The solid figure has a conical shape with a vertical side, which is the ordinate of the percentage of the total iron. Any horizontal section is a semi-lemniscate whose pointed corner rests on this ordinate. The curve of intersection between the surface of the cone and a vertical section, which also contains the iron ordinate, is an iso-silica curve. A point travelling along an iso-silica curve indicates that the percentage of the total phosphorus pentoxide increases with the soda/silica ratio, and as a result of phosphorus removal, the percentage of total iron in the slag decreases. The surface of the cone in Fig. 5*a* is the zone limiting the dephosphorizing reactions.

Along an iso-silica curve in section I (Fig. 5*b*), *e.g.*, about 25% SiO_2, for a given total iron, there is a point that gives the maximum percentage of phosphoric acid. The soda/silica ratio then decreases, because the percentage of the total sodium oxide in the slag decreases, and thus the percentage of phosphorus pentoxide also decreases. In Fig. 6, the percentage of the total sodium oxide is plotted against the total phosphorus pentoxide concentration in the slag. The experimental points, which belong to the silica section I, *i.e.*, below 25% silica, are close to the theoretical straight line representing sodium ortho-phosphate, Na_3PO_4. When the total silica is greater than 25 or 30%, the points (not shown in Fig. 6), lie haphazardly above the ortho-phosphate line.

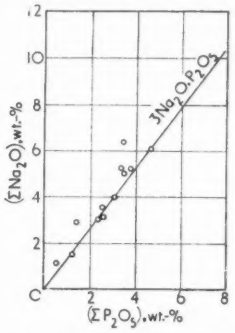


Fig. 6—Linear relation between ΣNa_2O and ΣP_2O_5 when ΣSiO_2 is less than 25%

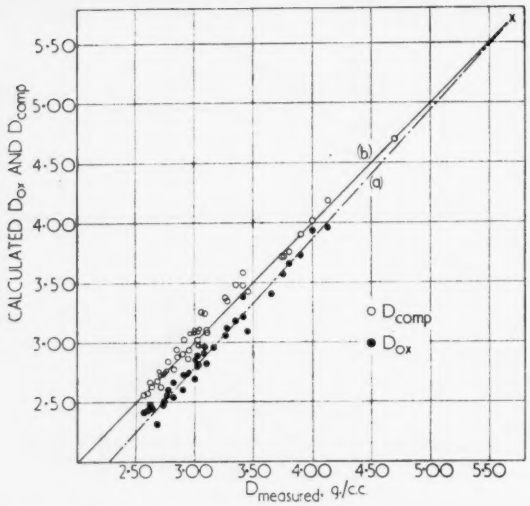


Fig. 7—Relationship between calculated and measured densities of soda-slags

SPECIFIC GRAVITY OF SODA-SLAGS

The specific volume of a substance is one of its fundamental properties, and is known to be partly additive and partly constitutive. In studying the properties of glass, numerous attempts have been made to correlate the densities and the compositions of glasses. It has been shown that within the narrow composition range of most soda–lime–silica glasses, the calculation of density by means of additive factors can give a fair approximation to that obtained by experiment. To account for deviations over a wider composition it has frequently been suggested that definite compounds exist in the glass, and that if the composition were expressed in terms of these compounds, the relationship between specific volume and composition would be truly linear. It was therefore considered that some useful information might be obtained on the constitution of soda-slags by determining their densities.

Method of Measurement

The procedure used for the density measurements was as follows :

A 100-mesh slag sample was dried at 110° C. for 1 hr. About 5 to 6 g. of the sample (weighed to a tenth of a milligram) were placed into a dry specific gravity bottle of known weight. The sample was well covered with medicinal paraffin, and placed in an evacuated desiccator for 4 hr. to remove all the air cavities. The bottle was filled up with medicinal paraffin, the glass stopper was inserted, and the bottle was immersed in a constant-temperature water bath. The temperature of the water bath was controlled by a toluene thermostat. During the actual measurements, the bath temperature was kept constant within the limits of $\pm 0{\cdot}1$° C. To ensure that all the measurements were made at a particular temperature, the bath was kept a few degrees above room temperature, and all the measurements were made at 28° C. The excess liquid, which came through the capillary of the glass stopper, was regularly wiped away while the bottle remained in the water bath. After careful wiping and drying, the bottle was weighed.

All measurements were made in duplicate, and the limit of deviation of each measurement from the mean was about 0·002 g./c.c. ; in many cases duplicates agreed to the third decimal place. Since soda-slags are partly soluble in water, medicinal paraffin was considered to be the most suitable liquid for this purpose. The specific gravity of the medicinal paraffin varied from 0·873 to 0·875 g./c.c.

Correlation Between Density and Slag Composition

In view of the additive and constitutive nature of the specific volume of substances, it was expected that some relationship would exist between the density and the composition of the system. Furthermore, the variation in density of the system will depend on the density and the amounts of each component present in the system.

The first method of approach is to assume that the

Table III

SPECIFIC GRAVITY OF SODA-SLAGS

Melt No.	D, g./c.c. at 28° C. $\pm$ 0·1° C.	D_{ox}, (Calc.) g./c.c.	D_{comp}, (Calc.) g./c.c.
*SA*1	3·260	3·058	3·373
*SA*2	3·161	2·956	3·429
*SA*3	3·080	2·917	2·930
*SA*4	3·085	2·962	3·237
*SA*5	3·058	2·976	3·250
*SA*6	3·275	3·114	3·347
*SA*7	3·000	2·688	3·100
*SA*8	3·026	2·881	3·092
*SA*9	3·037	2·805	3·110
*SA*10	3·019	2·818	3·209
*SA*11	2·943	2·730	2·860
*SA*12	2·776	2·599	2·845
*SA*13	2·739	2·504	2·746
*SA*14	2·732	2·471	2·736
*SA*15	3·101	2·985	3·098
*GA*2	2·950	2·747	2·930
*MA*1	2·621	2·474	2·665
*MA*2	2·681	2·309	2·674
*MA*3	3·028	2·787	2·970
*MA*4	3·450	3·084	3·429
*NS*1	3·650	3·407	3·402
*SH*1	2·710	2·625	2·721
*SH*2	2·761	2·556	2·760
*SH*3	2·630	2·453	2·632
*SH*4	2·566	2·412	2·561
*SH*5	2·603	2·431	2·568
*SH*7	2·819	2·665	2·778
*SH*8	2·698	2·647	2·750
*SH*9	2·851	2·751	2·883
*SH*10	2·825	2·536	2·683
*GH*1	3·355	3·176	3·486
*GH*2	3·100	2·820	3·081
*GH*3	2·887	2·612	2·900
*GH*4	2·905	2·714	3·020
*GH*5	2·849	2·743	2·944
*PGH*2	2·994	2·854	3·091
*PGH*3	2·956	2·933	3·075
*PMH*1	3·410	3·380	3·471
*PMH*2	4·702	4·698	4·690
*PMH*3	4·130	3·953	4·181
*PMH*4	4·003	3·925	4·016
*PMH*5	3·746	3·721	3·713
*MH*1	3·900	3·895	3·892
*MH*2	3·800	3·751	3·753
*MH*3	3·750	3·565	3·713
*MH*4	3·416	3·212	3·580

molten slag, whose constitution is retained at room temperature by air cooling, consists of oxides, *e.g.*, Na_2O, CaO, FeO, SiO_2, . . . etc., which form liquid solutions. In Fig. 7, D_{ox} is plotted against the actual density D of the slag. D_{ox} is calculated from the following equation :

$$D_{ox} = \frac{100}{\sum_1^n \frac{(ox)}{d_{ox}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where d_{ox}, n, and (ox) are the density, number, and weight percentage of the oxide respectively (*see* Table III). Although the relationship is linear (curve *a*), the calculated values of D_{ox} are noticeably lower than those determined. This may be attributed to the fact that, as a result of compound formation between these oxides, some shrinkage takes place, and consequently the densities calculated on the assumption that the slags consist of pure oxide mixtures are too low.

The second method of approach is to assume that the molten slags consist of certain compounds ; the theoretical density of the slag may then be found from the following equation :

$$D_{comp} = \frac{100}{\sum_1^n \frac{(comp)}{d_{comp}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where d_{comp}, n, and (comp) are the density, number, and weight percentage of the compound. The following compounds are assumed to exist in these slags :

Above 45% SiO_2—(Na_3PO_4), (Fe_2SiO_4), ($Na_2Si_2O_5$), ($CaSiO_3$), ($MnSiO_3$), ($MgSiO_3$), and ($Al_6Si_2O_{13}$)

Between 45 *and* 25% SiO_2—As above but with (Na_2SiO_3) instead of ($Na_2Si_2O_5$)

Below 25% SiO_2—(Na_3PO_4), (FeO), ($CaSiO_3$), (Mn_2SiO_4), (Mg_2SiO_4) and ($Al_6Si_2O_{13}$).

The graph in Fig. 7 is a straight line, passing through the origin of the co-ordinates, and with a slope of unity, *i.e.*, $D_{comp} = D$. This linear relationship indicates that ' packing effects,' involving the various ions and similar to those occurring in solid structures, are also present in the liquid state. Curve *a* approaches curve *b* as the density of the slag increases ; the intersection point of these lines may be taken as 5·70, which is the density of pure wüstite.

A simpler density/composition relationship is shown in Fig. 8, in which the $(\Sigma Fe)/(\Sigma SiO_2)$ ratio is plotted against the observed specific gravity D. The curve becomes a straight line when the value of the iron/silica ratio exceeds 2·10.

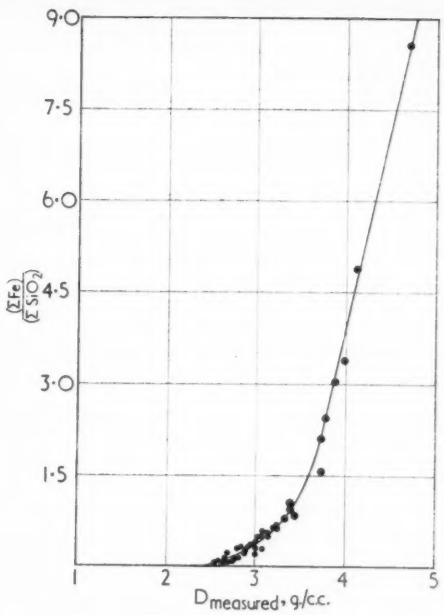


Fig. 8—Variation of specific gravity of slags with the iron/silica ratio

CONCLUSIONS

Dephosphorization

The careful study of the data on soda-slags so far available has revealed the greater stability of sodium ortho-phosphate compared with calcium ortho-phosphate, indicating that soda-slags can dephosphorize with much lower basicities than has been found possible in lime-slags. It is, however, necessary to maintain the slag composition within certain limits for the optimum elimination of phosphorus from iron. The acidity of soda-slags should be adjusted so that the formation of sodium silicates is possible. The oxidizing power and the availability of sodium oxide must be kept within favourable limits. It has been shown that the slag composition is related to the amount of phosphorus in the refined metal. A few postulations may be advanced from these considerations.

Phosphorus in iron (in solution or as iron phosphide) is oxidized to phosphorus pentoxide at the slag/metal interface. The phosphorus pentoxide is a strong acid, and therefore combines with a base to form the stable phosphate, under steelmaking conditions. These reactions may be represented by the following equations :

$$2Fe_3P + 5FeO \rightleftharpoons P_2O_5 + 11Fe \quad \ldots\ldots\ldots\ldots (5)$$

$$3(Na_2Si_nO_{2n+1}) + P_2O_5 \rightleftharpoons 2(Na_3PO_4) + 3nSiO_2 \ldots (6)$$

These reactions will proceed from left to right as the percentages of iron oxide and sodium silicates increase, and the available thermodynamic data indicate that an increase in temperature will shift the equilibrium to the left. The present experiments, however, do not show any noticeable effect of temperature on dephosphorization, although an increase in temperature will, for a given slag composition, increase the oxidizing power of soda-slags and will increase the amount of sodium oxide lost. The increased oxidizing power of the slag may not be followed by greater phosphorus removal. For example, in series *SH* the slags are definitely oxidizing, as is evident from the carbon content of the refined metal, but the reduction in phosphorus is small. This is attributed to the high silica concentration in the slag. Therefore, no advantage is gained by increasing the oxidizing power of the slag when no soda is available. Although sodium ortho-phosphate is a stable compound, its formation will be limited if silica is in excess (*see* equation 6). If the slag is neutral, with very little or no so-called ' free silica,' the reaction in equation (6) proceeds to

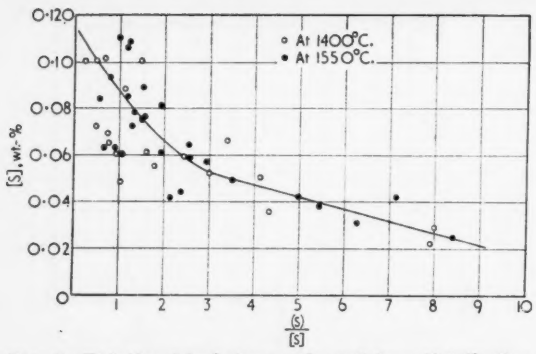


Fig. 9—Relationship between the sulphur distribution factor and sulphur

completion. This is the conclusion to be reached from the linear relationship in Fig. 6, *i.e.*, $(\Sigma Na_2O) = 1{\cdot}31(\Sigma P_2O_5)$. In high-silica slags, however, the relation becomes :

$$(\Sigma Na_2O) = 1{\cdot}31(\Sigma P_2O_5) + (Na_2O)_{SiO_2} \ldots\ldots (7)$$

The data indicate that the degree of phosphorus removal becomes less in the presence of sodium di-silicate. In other words, a greater reduction in phosphorus may be attained when the soda/silica ratio is such that sodium meta-silicate forms. The suggestion that this behaviour is attributable to a greater stability of the di-silicate is open to criticism because the melting point and the heat of formation of sodium di-silicate are appreciably lower than those of the sodium meta-silicate. An alternative explanation is based on the hypothesis of the ionization of slags. There are definite indications that molten slags dissociate into their ions; thus, in a sodium silicate system, the space available for phosphate anions is fixed by the sodium and silicate ions, and so by increasing the soda/silica ratio the percentage of silicate anions will decrease, and consequently, more phosphate anions can be taken into the system. The characteristics of the limiting surface (*see* Fig. 5*b*) support this explanation : at a given point either a dephosphorizing or a rephosphorizing reaction will occur, until the composition of that point falls on to the surface of the cone, *i.e.*, the limiting surface.

Desulphurizing Under Soda-Slags

Although desulphurization under soda-slags has not been investigated in the present tests, a reduction of 0–90% of the sulphur content of the iron has been generally observed. In Fig. 9 the percentage of sulphur in the refined metal is plotted against the sulphur distribution factor, (S)/[S]. The experimental points obtained from 1400 and 1550° C. melts are rather scattered, but the direction of their location agrees well with the known fact that the distribution factor increases as the percentages of sulphur in the iron decrease. Apart from this simple relationship, great difficulty has been experienced in determining how this reaction is controlled by the slag composition. A large number of variables, which are directly or indirectly connected with the desulphurizing reaction, have been considered without success. Since no definite correlations have been found in this work, it is assumed that the experimental procedure was not ideal for the study of desulphurization because the sulphur pick-up varied from melt to melt.

Possible Applications of Soda-Slags

In considering the possible applications of soda-slags in practice, the following three conditions must be fulfilled :

(i) The slags must contain a sufficient amount of silica to retain a reserve of soda
(ii) The total silica and the total soda contents of these slags have a very noticeable effect on the amount of phosphorus that can be removed from iron
(iii) The slags must be oxidizing.

If a very high percentage reduction in phosphorus is required, *e.g.*, $>90\%$, then the slag must not contain more than 25–30% of silica. In these slags the amount of soda required can be adjusted by the amount of phosphorus to be removed from the metal. It will generally not exceed 10%. The main difficulty in adjusting the composition of these slags is the choice of the other bases. For instance, large lime additions cannot be made because of their effect on soda ; on the other hand it is neither economical nor practicable to introduce other bases in place of lime, *e.g.*, oxides of iron, manganese, or magnesium. The slags that brought about the best phosphorus removal, down to 0·02–0·01% of phosphorus, contained large percentages of iron (*see* Table II) and cannot be considered suitable for practical application.

For a 50–80% reduction in phosphorus, the total silica in the slag should range from 40 to 35%, respectively. If required, the slags can retain high percentages of soda (15–20%). The oxidizing conditions in these slags are believed to be sufficiently high for a 50–80% phosphorus reduction from a phosphoric pig iron. Since these slags have serviceable fluidities at temperatures as low as 1400° C., and the carbon in the semi-refined iron can be kept as high as 1·5–2·0%, the soda-slags within this range appear to have an important practical use in the 'mixer.' The soda-neutral slags are most suitable and a 1·0–1·5% phosphorus charge may be dephosphorized by 50–80% at 1400° C.

Although the soda-acid slags, 50–60% silica, cause a 40–15% reduction in phosphorus, their application becomes rather limited. In spite of this, however, they may still be applied in acid processes, provided that the original phosphorus in the charge is low.

Acknowledgments

The authors wish to thank their colleagues at Sheffield University for many helpful discussions, and in particular Dr. J. White, for willing criticism.

Dr. Turkdogan is most appreciative of the financial assistance given him through the Andrew Carnegie Fund of The Iron and Steel Institute.

References

1. W. R. MADDOCKS and E. T. TURKDOGAN : *J. Iron Steel Inst.*, 1949, vol. 162, pp. 249–264.
2. W. OELSEN and H. WIEMER : *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1942, vol. 24, pp. 167–210.
3. W. OELSEN and H. MAETZ : *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1941, vol. 23, pp. 195–245.
4. P. T. CARTER : *J. Iron Steel Inst.*, 1950, vol. 166, pp. 321–322.

X-Ray Investigation of the Epsilon Phase in an Fe–Mn Alloy

By J. Gordon Parr, B.Sc.

SYNOPSIS

X-ray investigation confirms that the ϵ phase has a close-packed hexagonal structure, but refutes a previously assumed crystallographic relationship between the γ and ϵ phases. The relative amounts of the α, γ, and ϵ solid solutions in heat-treated powder specimens have been determined by an X-ray method, and have led to the conclusion that the ϵ phase is produced by a process of athermal nucleation; it is not an equilibrium phase.

Introduction

THE ε phase was first discovered in iron–manganese alloys by Schmidt,[1] who showed, by X-ray diffraction methods, that it was a close-packed hexagonal structure, which might exist over a range of composition 11·8% to 29% of manganese. In an effort to locate the ε phase-field, Schmidt prepared small needles of alloys of appropriate composition and quenched them from temperatures of 800°, 1000°, and 1300° C., into iced water; but subsequent X-ray examination invariably showed the ε phase associated with the cubic phases of the iron–manganese solid solution.

Öhman[2] took X-ray photographs of suitable alloys at temperatures between 500° and 1000° C., but in none of them was the ε phase—free or associated—detected. He suggested that the phase was produced only by quenching, that it was unstable, and that it arose from a breakdown of the γ solid solution, decomposing itself to reproduce γ or to give a body-centred cubic phase α', supersaturated in manganese.

Ôsawa[3] and Ishiwara,[4] on the evidence of dilatometric and X-ray examination, suggested that the ε phase was located about an intermetallic compound (Fe_5Mn) and was derived from a peritectoid change, which occurred at a temperature of 200° C. and at a composition of 20% of manganese.

Walters and co-workers,[5, 6] using purer materials than earlier investigators, confirmed the existence of the ε phase, not only by X-ray and dilatometric measurements but also magnetically and microscopically. They recorded that ε was produced by cooling solid specimens slowly, as well as by quenching them, from temperatures above 900° C., and that it reverted to the γ solid solution when it was heated to temperatures above 200° C. By cold-working a 20% Mn alloy which had been furnace-cooled, it was possible to attain complete transformation to ε. Walters concluded that the ε phase might be produced by a peritectoid reaction; as an intermediary in the $\gamma \rightarrow \alpha$ change; or as a transition phase.

The latter theory was also held by Bain, Davenport, and Waring,[7] who, working with alloys of commercial purity, observed that ε could be removed in some alloys by cold-working and annealing at "a temperature below the lowest critical point."

Most of the work outlined above involved solid specimens, which not only attain equilibrium slowly but are less able to accommodate pressure changes that may be induced by structural transformations. Scott[8] pointed out that a reaction such as $\gamma \rightarrow \varepsilon$, which is accompanied by a volume decrease, is aided by pressure. Therefore, it is probable that unrelieved cooling stresses in a solid specimen induce an internal pressure and so favour the formation of the ε phase.

No work on the ε phase appears to have been published since 1936, and it seemed desirable to reopen the investigation. It was decided to apply X-ray methods to powders in which, it was hoped, there would be no complications due to imposed pressure effects and there would be a greater chance of attaining equilibrium.

MATERIALS

Three 100-g. ingots, containing 12·2%, 15·5%, and 18·5% of manganese, respectively, were made up from Johnson Matthey iron (*J.M.* 845) and manganese (*J.M.* 810). The materials were charged into an alumina crucible held within an induction coil, and were heated to a temperature just below their melting-points in a stream of hydrogen from which oxygen had been removed by palladiumized asbestos. Melting and cooling were effected in argon, which had first been passed over red-hot calcium to eliminate nitrogen. Each ingot was homogenized in argon at 1150° C. to produce a structure which chemical analysis and microscopic examination showed to be uniform.

All the work described in this paper was performed on the 18·5% Mn ingot, which contained 0·0055% of carbon and 0·0245% of aluminium.* Experiments made on the other two alloys were corroborative.

THE CRYSTAL STRUCTURE OF THE ε PHASE

To determine the crystal structure of the original alloy, a 0·6-mm. dia. needle was turned from part of the ingot and was deeply etched to remove the cold-worked layer. The specimen, like all the others investigated, was mounted in a 19-cm. Debye-Scherrer camera and was irradiated with Fe-K_α radiation. The γ and ε phases only were found to be present,

Manuscript received 11th May, 1951.

Mr. Parr is Lecturer in the Department of Metallurgy, the University of Liverpool.

* The carbon and aluminium determinations were made by the National Physical Laboratory.

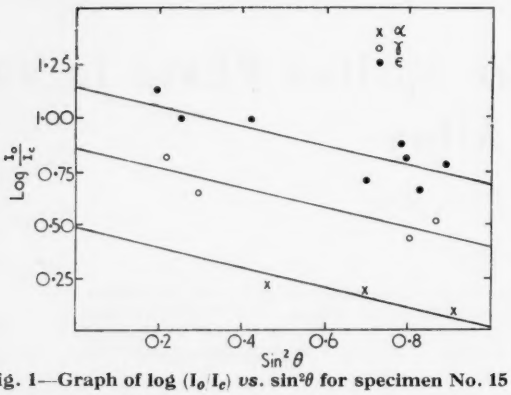


Fig. 1—Graph of log (I_o/I_c) *vs.* $\sin^2\theta$ for specimen No. 15

and values of $\sin^2\theta$ and intensity measurements confirmed that the structure of ε was close-packed hexagonal. The lattice parameters of the phases, corrected by the methods described by Nelson and Riley[9] and Taylor and Floyd,[10] were :

$a_\gamma = 3{\cdot}585$ Å.

$a_\epsilon = 2{\cdot}530$ Å., $c_\epsilon = 4{\cdot}079$ Å., $c/a = 1{\cdot}612$.

As previous workers have noted, there is an apparent coincidence of the lines from the planes $(220)_\gamma$ and $(110)_\epsilon$. The similarity between the face-centred cubic and the close-packed hexagonal arrangements, and consequently the ease of transformation $\gamma \rightleftharpoons \varepsilon$, was pointed out by Schmidt[1] and subsequent workers. Bain, Davenport, and Waring[7] suggested that when the *ABABAB* . . . arrangement of close-packed hexagonal layers transforms to the *ABCABC* . . . arrangement for face-centred cubic packing, it requires a change in position of only two-thirds of the atoms, and such a movement might be easily accommodated. This hypothesis, however, would demand coincidence of $(111)_\gamma$ and $(002)_\epsilon$—which certainly does not occur. The only evidence in support of any simple transformation in which some atoms retain their original positions is the coincidence of the diffraction lines from $(110)_\epsilon$ and $(220)_\gamma$; but in a powder photograph coincident lines from two sets of planes merely indicate equal spacings between the respective planes. However, there is not even exact equality between the spacings of the planes $(220)_\gamma$ and $(110)_\epsilon$ as calculated from the lattice parameters given above :

Spacing between $(220)_\gamma$ planes $= a_\gamma/\sqrt{2} = 2{\cdot}535$ Å.
Spacing between $(110)_\epsilon$ planes $= a_\epsilon = 2{\cdot}530$ Å.

This discrepancy is further borne out by the fact that the intensity curve of the double diffraction line is broadened about a vertical line drawn through its peak—indicating that it is composed of two non-coincident curves.

The discrepancies in calculated spacings, and in the intensity curve, are also observed in powder specimens in which the γ and ε phases are produced by quenching. There is, therefore, no evidence to show that the atom shift involved in a supposed $\gamma \rightleftharpoons \varepsilon$ transformation is so simple as that proposed by earlier workers ; on the contrary, the change would involve some movement of all atoms. It is misleading to suggest that, owing to their similar atomic arrangements, the face-centred cubic and close-packed hexagonal structures could easily be formed one from the other.

THE FORMATION OF THE ε PHASE

Method of Investigation

Powder specimens of the alloy were given different heat-treatments, and the change in the amounts of the phases present was computed. Hence, the conditions that affected the production of ε were categorized and it became possible to deduce the mechanism of its formation. The crux of the technique was the determination of the amounts of phases present in the heat-treated powder samples. For this, the method that Lipson and Stokes[11] adopted in their work on the crystal structure of graphite was used, because the scattering powers of iron and manganese atoms are much the same, and therefore the composition of a phase does not affect the intensity of the diffracted X-ray beam.

In this method, a powder photograph is taken of the sample, the intensities of the diffraction lines are measured, and log (I_o/I_c) is plotted against $\sin^2\theta$ for each of the patterns (where I_o is the observed intensity of a diffraction line and I_c is the calculated intensity). Each pattern yields a number of points which lie on a straight line (as was shown by Bradley and Lu[12]), and the lines obtained for a phase mixture in any particular specimen will be parallel. A typical set of results is plotted in Fig. 1. The logarithmic ratio of the amounts of the phases present is given by the relative intercepts of the three lines on the ordinate. Therefore, by taking antilogarithms of these values, the relative amounts of the phases α, γ, and ε may be calculated.

This technique, however, is lengthy, and so that a large number of specimens might conveniently be examined it was assumed that the slope of the lines on the graph would be the same for all specimens that were made similarly and were of the same alloy. This assumption leads to small errors, but these are

Table I

AMOUNTS OF PHASES PRESENT AFTER ANNEALING

Specimen Number	Annealing Temperature, °C.	Annealing Time, hr.	Amount of Phase, % (approx.)		
			c_α	c_γ	c_ϵ
0	Needle specimen from ingot		0	12	88
1	Filings cut from ingot		0	0	100
2	150	500	4	26	70
3	150	1000	16	44	40
4	240	500	24	38	38
5	240	1000	17	46	37
6	450	¼	20	80	0
7	450	½	22	78	0
8	450	1	19	81	0
9	450	24	22	78	0
10	450	48	24	76	0
11	600	5	25	75	0

not significant in an investigation such as this, where figures are intended only to indicate general trends. Accordingly, an X-ray photograph of each specimen was taken and the intensity of one chosen diffraction line from each pattern was measured. Thus, values of log (I_o/I_c) when $\sin^2\theta = 0$ could be calculated (*see* Fig. 1). For each film, three such values were obtained —one for each phase present—and the relative amounts of α, γ, and ε were deduced and expressed as percentages c_α, c_γ, and c_ϵ (*see* Table I).

The powder samples were cut from the ingot with a fine file andwere heat-treated in an atmosphere of argon ; they were then packed, unsieved, into cellophane tubes of 0·5 mm. bore, for X-ray examination. Chemical analyses of selected powders showed that the manganese content was never appreciably reduced as a result of heat-treatment. The lowest figure recorded was 17% of Mn. Because of their strength and isolation, the diffraction lines chosen to represent their respective phases were : (211) for α, (200) for γ, (101) for ε.

RESULTS OF THE INVESTIGATION

The filed, unannealed powder contained only the ε phase (*see* Table I). The annealing treatments at temperatures between 150° and 600° C. reduced the amount of ε, which dissociated into both α and γ phases. Water-quenching the powder from temperatures above 750° C. produced the ε phase in an amount which increased as the quenching temperature was raised to 1350° C., but on quenching from 1350° C. the specimen became entirely body-centred cubic (*see* Table II). The effect of tempering two quenched samples at 450° C. is shown in Table III. Before the ε phase was destroyed, it increased appreciably in amount ; this effect is also demonstrated in Table IV, which gives the results of tempering quenched specimens at 240° C. Quenching in liquid nitrogen produced much the same amount of ε as did water-quenching from the same temperature (*see* Table V), but, again, considerably greater amounts of ε were formed on subsequent tempering. The effect of cold-working and annealing a quenched sample is illustrated in Table VI ; cold work increased the amount of ε, but hastened its subsequent decomposition. Table VII shows the results of cooling the powder slowly from elevated temperatures ; air-cooling from above 750° C. nearly always produced γ, but occasionally some ε was formed.

Öhman[2] has already shown that ε does not exist at temperatures between 500° and 1000° C. ; in confirmation of his results, an X-ray photograph taken at 950° C. showed no diffraction lines from the ε phase.

Table II

AMOUNTS OF PHASES PRESENT AFTER WATER-QUENCHING

Specimen Number	Quenching Temperature, °C.	Amount of Phase, % (approx.)		
		c_α	c_γ	c_ϵ
12	750	81	19	0
13	900	0	95	5
14	1050	12	68	20
15	1250	15	30	55
16	1350	100	0	0

Table III

AMOUNTS OF PHASES PRESENT AFTER TEMPERING AT 450° C. FOLLOWING WATER-QUENCHING

Specimen Number	Tempering Time, hr.	Amount of Phase, % (approx.)		
		c_α	c_γ	c_ϵ
Water-quenched from 1050° C.				
14	As-quenched	12	68	20
24	½	0	76	24
25	1	13	70	17
26	1½	10	80	10
27	6	25	67	8
28	24	31	64	5
Water-quenched from 1250° C.				
15	As-quenched	15	30	55
17	¼	11	29	60
18	½	8	21	71
19	1½	14	22	64
20	3	27	22	51
21	6	24	36	40
22	24	37	34	29
23	100	42	32	26

DISCUSSION OF RESULTS

To produce ε in the powder it is necessary to cool the specimen rapidly from a temperature above 750° C., but the possible implication that ε may be a high-temperature phase is disproved by high-temperature X-ray examination. The peculiar formation of a body-centred cubic phase on quenching from 1350° C. is not yet understood, and is the subject of further research. Tempering any powder specimen that has been quenched from above 750° C. (even the one quenched from 1350° C.) results in an initial increase in the amount of ε, followed by its decomposition. These facts may be best explained on the basis of the theory of athermal nucleation put forward by Fisher, Hollomon, and Turnbull.[13] Adapting this theory to the formation of the ε phase, the following argument is proposed.

At temperatures between 750° and 1350° C., when the alloy is a face-centred solid solution, there also exist embryos of a hexagonal phase. Each embryo has a hexagonal arrangement of atoms, and at the temperature of its environment is of a characteristic sub-critical size—that is, it cannot accept and retain atoms to become a nucleus. When the alloy is quenched, however, the embryos remain at sensibly the same size, which at the reduced temperature is greater than critical. They are 'automatically promoted to nuclei,' and can grow. Growth occurs to some extent during quenching, but presumably would not occur if the rate of cooling were infinitely great. When quenching is made more severe, more embryos should be retained, and therefore a greater amount of the ε phase would be produced on subsequent tempering. This is shown to occur when a specimen is quenched in liquid nitrogen ; on tempering, the

Table IV

AMOUNTS OF PHASES PRESENT AFTER TEMPERING AT 240° C. FOLLOWING VARIOUS QUENCHING TREATMENTS

Specimen Number	Quenching Temperature, °C.	Quenching Medium	Tempering Time, hr.	Amount of Phase, % (approx.)		
				c_α	c_γ	c_ε
14	1050	Water	Nil	12	68	20
31	,,	,,	50	0	80	20
32	,,	,,	500	0	83	17
15	1250	Water	Nil	15	30	55
33	,,	,,	50	0	24	76
34	,,	,,	500	18	23	59
16	1350	Water	Nil	100	0	0
35	,,	,,	50	94	0	6
36	,,	,,	500	83	0	17
29	900	Liquid N_2	Nil	0	95	5
37	,,	,, ,,	50	0	77	23
38	,,	,, ,,	500	0	39	61
39	,,	,, ,,	1000	5	50	45
30	1050	Liquid N_2	Nil	0	83	17
40	,,	,, ,,	500	4	40	56

specimen yields more ε than one that has been water-quenched from the same temperature and tempered under similar conditions (*cf.* 32 and 40, Table IV).

Table II shows that quenching immediately from a high temperature produces more ε than quenching from a lower one, owing to either the presence of more ε embryos at the higher temperature, or a greater opportunity for growth during quenching. Comparison of the data in Table III, however, shows that the specimen quenched from a higher temperature not only contains more ε but yields more during tempering, thus proving that more nuclei, and hence more embryos, were initially present.

Tables III and IV show that, once nucleated, ε may grow at the expense of either or both of the cubic phases. After a maximum quantity of ε has been formed the phase breaks down, rapidly at first and then more slowly. The decreasing rate of decomposition is to be expected, because the regions of ε become smaller as their stability increases. A similar condition exists in the disordering of an ordered solid solution. As the ε phase decomposes during tempering, there is always an increase in the amount of α in the alloy. There is no consistent alteration in the amount of γ. The figures show considerable scatter, which might be accounted for by the approximate nature of the method of estimation, and also by unavoidable variations in the heat-treatment of a series of specimens. Nevertheless, it may be concluded that at temperatures of 240° and 450° C. ε breaks down to produce only the body-centred cubic phase.

The remaining fact to be explained is that although the phase is unstable at the tempering temperatures, as is shown by its eventual decomposition, it initially increases in amount. This could be because the precipitated phase possesses a different crystal structure from the original α phase, and hence requires thermal nucleation. The ε phase could grow upon

Table V

AMOUNTS OF PHASES PRESENT AFTER QUENCHING IN LIQUID NITROGEN

Specimen Number	Tempering Temperature, °C.	Amount of Phase, % (approx.)		
		c_α	c_γ	c_ε
29	900	0	95	5
(*cf.* 13	900° C. water-quenched	0	95	5)
30	1050	0	83	17
(*cf.* 14	1050° C. water-quenched	20	68	12)

Table VI

AMOUNTS OF PHASES PRESENT AFTER QUENCHING, COLD-WORKING, AND ANNEALING

Specimen Number	Treatment	Amount of Phase, % (approx.)		
		c_α	c_γ	c_ε
15	Water-quenched from 1250° C.	15	30	55
41	Specimen 15 cold-worked*	0	20	80
42	Specimen 41 annealed at 450° C. for ½ hr.	28	40	32
cf. 18	Water-quenched from 1250° C. and tempered at 450° C. for ½ hr.; not cold-worked	8	21	71

* By rubbing the powder between two file faces

the already existing crystals, and would decompose only after stable nuclei of the new phase had been established. There is, however, no evidence to support such a theory, since the phase formed when ε decomposes is identical in structure and parameter to the original α phase.

Alternatively, if the breakdown of ε were associated with the formation of a body-centred cubic phase of different composition α′ (as Schmidt[1] suggested), then the free-energy relationship between α, γ, and ε, which during the first stages of tempering favours the formation of ε, may become altered and allow the precipitation of α′. This type of mechanism has been discussed by Lipson and Weill[14] in their work on the η phase in the iron–silicon system. Whereas in iron–silicon alloys changes in composition are readily detected by an alteration in lattice parameter, the similarity between the atomic radii of iron and manganese atoms makes this impracticable in the iron–manganese system. At present, therefore, there are insufficient data to substantiate this theory.

The important part that pressure plays in the formation and decomposition of the ε phase is illustrated by the effect of annealing and tempering stressed powders. Table I shows that annealing a stressed powder at temperatures between 150° and 600° C. results in the immediate decomposition of ε. An additional complication arises, in that the stressed powder consists of 100% ε before annealing. However, the effect of imposed stress, in initially increasing the percentage of ε in the powder and producing its immediate breakdown on subsequent heat-treatment, is confirmed by data in Table VI.

It seems significant that the lower limit of quenching temperature (between 750° and 900° C.) which produces ε coincides with the $\alpha \rightarrow \gamma$ A_c temperature. This may indicate that embryos of ε can exist only in an environment of the γ solid solution. For confirmatory evidence, a powder specimen (No. 46) was cooled from 1050° to 550° C. at a rate that would retain γ but would not 'freeze' ε embryos of a size characteristic to 1050° C. The specimen was water-quenched from 550° C., and ε was produced, indicating the presence of ε embryos at a temperature of 550° C. in an environment of face-centred cubic phase.

Table VII

AMOUNTS OF PHASES PRESENT AFTER CONTROLLED COOLING TREATMENTS

Specimen Number	Treatment	Amount of Phase, % (approx.)		
		c_α	c_γ	c_ϵ
43	Air-cooled from 1050° C. to room temperature	0	100	0
44	Specimen 43 tempered at 450° C. for ½ hr.	0	100	0
45	Cooled at 12° C./min. from 1050° to 750° C., and then air-cooled to room temperature	0	100	0
46	Cooled at 40° C./min. from 1050° to 550° C., and then water-quenched	88	0	12

CONCLUSIONS

At this stage in the investigation of the ε phase, the following conclusions may be drawn :

(1) The ε phase occurs in an iron–manganese alloy of high purity containing 18½% of manganese. It has a close-packed hexagonal structure.

(2) There is no exact equality of interplanar spacing between major crystallographic planes in the γ and ε phases ; therefore, it cannot be assumed that a simple $\gamma \rightleftharpoons \varepsilon$ transformation takes place.

(3) In powder specimens, the ε phase is produced only by rapid cooling from the γ range of the constitutional diagram ; the evidence offered by quenching and tempering treatments indicates that it is athermally nucleated and is not an equilibrium phase.

(4) Tempering a quenched powder at temperatures up to 450° C. brings about an initial increase in the amount of ε, at the expense of either or both of the cubic solid solutions ; but continued treatment destroys the ε phase and produces a stable body-centred cubic phase.

(5) The effects of imposed stress on the formation and decomposition of the ε phase have not been fully investigated. However, cold work increases the amount of ε (confirming Walters[5]), and causes its rapid destruction on annealing (confirming Bain, Davenport, and Waring[7]).

(6) A body-centred cubic structure has been produced on quenching a powder from 1350° C., and is being investigated.

Acknowledgments

The author wishes to thank Dr. H. Lipson for his advice in the interpretation of the X-ray results ; Dr. W. S. Owen for his helpful criticism at all stages of the work ; and Dr. S. J. Kennett for his interest and encouragement.

References

1. W. Schmidt : *Arch. Eisenhüttenwesen*, 1929–30, vol. 3, pp. 293–300.
2. E. Öhman : *Zeitschrift für physikalische Chemie*, 1930, vol. 8, B, pp. 81–110.
3. A. Ôsawa : *Science Reports of the Tôhoku Imperial University, Sendai*, 1930, vol. 19, pp. 247–264.
4. T. Ishiwara : *Ibid.*, pp. 499–519.
5. F. M. Walters, Jr. : *Transactions of the American Society for Steel Treating*, 1931–32, vol. 19, pp. 577–621.
6. V. N. Krivobok and others : *Ibid.*, 1933, vol. 21, pp. 807–864.
7. E. C. Bain, E. S. Davenport, and W. S. N. Waring : *Trans. Amer. Inst. Min. Met. Eng.*, 1932, vol. 100, pp. 228–249, *Tech. Publ.* No. 467.
8. H. Scott : *Ibid.*, 1931, Iron and Steel Division, pp. 284–300, *Tech. Publ.* No. 435.
9. J. B. Nelson and D. P. Riley : *Proc. Phys. Soc.*, 1945, vol. 57, pp. 160–177.
10. A. Taylor and R. W. Floyd : *Acta Crystallographica*, 1950, vol. 3, pp. 285–289.
11. H. Lipson and A. R. Stokes : *Proc. Roy. Soc.*, 1942, vol. 181, Series A, pp. 101–105.
12. A. J. Bradley and S. S. Lu : *Zeitschrift für Kristallographie*, 1937, vol. 96, pp. 20–37.
13. J. C. Fisher, J. H. Hollomon, and D. Turnbull : *J. Appl. Phys.*, 1948, vol. 19, pp. 775–784.
14. H. Lipson and A. R. Weill : *Trans. Faraday Soc.*, 1943, vol. 39, pp. 13–18.

Related Diffusion Effects of Carbon and Sulphur in Iron at High Temperatures

By K. J. Irvine, B.Sc., Ph.D.

SYNOPSIS

Experiments have been carried out to determine the conditions under which large-scale penetration of iron sulphide into iron takes place in the form of a molten iron–iron-sulphide eutectic. The process has been shown to apply generally to metals that can form interstitial solid solutions, and under conditions involving the inward diffusion of an element in interstitial solid solution.

It has been demonstrated that sulphur is appreciably soluble in iron containing manganese and nickel, and a further study has been made of the related diffusion effects of carbon and sulphur in iron at temperatures above 1000° C. That precipitation of manganese sulphide particles at the austenite grain boundaries is responsible for the overheating of steel has been confirmed, and several changes which lead to burning have been described.

In a previous paper,[1] certain observations were made on the penetration of iron sulphide into iron under carburizing conditions. It was suggested that at temperatures high enough for the formation of a molten iron–iron-sulphide eutectic, and under the influence of a carbon concentration gradient, iron sulphide formed the molten eutectic with iron and then penetrated into the iron by a continuous solution of iron at the inner face and by the removal of the iron from solution by carburization at the outer face. In this way a definite band of iron sulphide was made to move inwards into the iron.

The present investigation has been carried out to determine whether other elements in interstitial solid solution, such as nitrogen or hydrogen, act in a similar way and whether such a movement can take place through other metals. In ferrous metallurgy irons containing local concentrations of carbon and sulphur are often subjected to high temperatures and the possible movements of these two elements during high-temperature heat-treatment have been investigated.

EXPERIMENTS WITH IRON

As in the earlier work specimens of Armco iron were coated with a paste of iron sulphide and Bakelite cement, and were then subjected to the appropriate atmosphere (carbon monoxide, hydrogen, or nitrogen) at 1000° C. for varying periods.

Hydrogen Atmosphere

No large-scale penetration of iron sulphide was found, although the outside rim of the specimen had been embrittled and tended to break away at the grain boundaries during polishing. Very careful polishing revealed some very fine films of iron sulphide around the grain boundaries. Increased time of treatment resulted in a greater depth of this embrittled rim.

Nitrogen Atmosphere

A small amount of iron sulphide had penetrated into the iron. The sulphide was located entirely at the grain boundaries. For any similar period of heating, the depth of penetration was deeper than with hydrogen, and comparable with that obtained with carbon monoxide. The amount of sulphide was small and no definite band was formed. Since pure nitrogen is a poor nitriding agent, an experiment was carried out using ammonia, which is a more effective nitriding agent. The amount of penetration was very much greater and more nearly comparable with that obtained using carbon monoxide.

EXPERIMENTS WITH OTHER METALS

Similar experiments were carried out with other metals which could take carbon, nitrogen, and hydrogen into interstitial solid solution.

Nickel

Experiments using nickel coated with nickel sulphide showed that extensive penetration by nickel sulphide could be obtained in atmospheres of hydrogen, carbon monoxide, and nitrogen ; the effect was greatest with nitrogen. Small sulphide particles were concentrated within the grains, beyond the limit of grain-boundary penetration. This effect tended to be masked by the large amounts of nickel sulphide. Duplicate experiments were therefore carried out in the three atmospheres using nickel specimens coated with iron sulphide. Figures 1 and 2 show similar structures, which are more easily distinguished. The greatest depth of penetration was obtained using nitrogen ; there was more sulphide at the grain boundaries, and the small particles were easily visible at a magnification of 40. The effect was similar with carbon monoxide, but there was less depth of penetration, less sulphide at the grain boundaries, and the sulphide particles within the grains were smaller than with nitrogen. In hydrogen atmospheres, penetration was confined entirely to the concentration of small sulphide particles within the grains. With nitrogen the particles were visible at a magnification of 40, whereas with hydrogen

Manuscript received 3rd May, 1951.

Dr. Irvine is Lecturer in Metallurgy at the University of Leeds.

the particles were visible only at the highest magnification ; no general idea of the structure could be obtained until the specimen was etched, when the sulphide particles were attacked preferentially. Treatment periods of more than 50 hr. showed that the zone of small sulphide particles moved into the metal as the time of treatment increased. Specimens heated in a vacuum showed a slight diffusion of sulphur, appearing as a fine dispersion of sulphide particles, and an even smaller depth of penetration than that obtained with hydrogen.

Copper

Experiments using copper, which does not form interstitial solid solutions, showed no penetration, the sulphide remaining on the surface of the treated specimen. Penetration of sulphur therefore takes place only with metals capable of taking hydrogen, carbon, and nitrogen into interstitial solid solution.

Monel

Monel metal, having a lattice similar to that of nickel, was able to take up the interstitial hydrogen, carbon, and nitrogen, and penetration of sulphide took place (*see* Fig. 3). The sulphide, which precipitated, formed copper sulphide ; at the grain boundaries the large amount which precipitated exhausted the local copper content, and pure nickel could be distinguished as a separate phase. Within this region some nickel sulphide was also observed.

The main difference between the penetration of nickel and Monel metal and that of iron was the association of the fine sulphide particles with the larger sulphide penetration. If it is assumed (and most published work supports this) that sulphur has a very small solubility in iron, then it would be expected in these experiments that the iron sulphide penetrated by dissolving iron, but that the penetrating sulphide remained as a compact band because there is no tendency for the sulphur to go into solution in the iron. Results for nickel, however, suggest that sulphur is appreciably soluble in nickel and that this solubility is affected by the element in interstitial solid solution. Thus, when nitrogen is the element in solution, a considerable amount of the sulphide is forced to the grain boundaries, whereas with hydrogen, which has an atom size very much smaller than nitrogen, this is not the case.

Plain Carbon Steels

In the previous paper[1] an example was reported in which a fine dispersion of sulphide particles, similar to that occurring in nickel, was obtained with a plain carbon steel. This steel differed from the iron used in the present experiments because it had an initial carbon content, and certain elements, notably manganese and silicon, were present in substitutional solid solution. Many experiments with pure iron containing carbon additions showed that although an initial carbon content slowed down the rate of penetration and tended to make the penetrating band discontinuous, it did not produce the fine dispersion of sulphide particles. The presence of carbon in the plain carbon steel could not, therefore, account for this structure. Further experiments demonstrated, however, that when additions of other elements, notably manganese and nickel, were made to otherwise pure iron, the penetrating sulphide was associated with the fine dispersion of sulphide particles (*see* Fig. 4). This also indicates that the presence of manganese or nickel increases the solubility of sulphur.

Formation of Sulphide Particles

Many of the small sulphide particles existed, at the temperature of treatment, at the centres of regions of iron high in sulphur. Their exact shape and distribution depended on the carbon content of the iron and the rate of cooling after heat-treatment. Quenching experiments showed that the amount of sulphur in solution decreased as the carbon content increased. The sulphur coming out of solution appeared as very much smaller sulphide particles surrounding the particles which existed at the treatment temperature. With slow cooling, the sulphur coming out of solution precipitated on the already existing particles. The same effect was found with nickel and Monel metal. When the carbon (or nitrogen) content increased in the areas containing sulphur in solution, some sulphide was precipitated both within the grains and at the grain boundaries. This continued until there was no sulphur left in solution. Additional evidence of the effect of the interstitial element in solution in the metal was shown by the experiments using nickel in atmospheres of hydrogen, carbon monoxide, and nitrogen. The sulphide particles were larger for gases of larger atom size.

RELATIVE MOVEMENT OF CARBON AND SULPHUR AT HIGH TEMPERATURES

To investigate the relative movements of carbon and sulphur, steel specimens coated with iron sulphide were subjected to a carburizing atmosphere, which produced a structure consisting of manganese sulphide particles surrounded by a high carbon concentration. The analysis of the steel used (steel *A*) was : 0·76% C, 0·28% Si, 0·59% Mn, 0·026% S, 0·032% P. In this steel the zone of sulphide particles was localized and was easily distinguished from the areas not containing any sulphide particles.

Carbon Steel in Carbon Monoxide

In a carbon monoxide atmosphere a pressure of carbon was maintained in the specimen. Specimens of steel *A* heated at temperatures between 1000° and 1300° C. showed that there was a high carbon concentration surrounding the larger sulphide particles, and therefore only a small carbon concentration gradient existed. Under these conditions there was little possibility of iron forming a molten eutectic with the sulphide. The large sulphide particles moved slightly inwards but small sulphide particles which surrounded these larger particles tended to disperse, increase in size, and to move towards the centre of the specimen. This effect was initially only slight at 1000° C. but after 500 hr. more dispersion occurred. As the temperature was raised this effect became more apparent, and the dispersion moved into the metal. At 1000° C. these small particles appeared in distinct groups, suggesting that at this temperature considerable heterogeneity existed in the distribution

of carbon and sulphur, but if the time of treatment was increased considerably, or if the temperature was increased to about 1300° C., this distribution became more uniform, and the rate of movement increased.

As the temperature was raised to 1200° C., although a carburizing atmosphere was maintained, the part of the specimen containing the high concentration of sulphide particles had a lower carbon content than either the edge or the centre of the specimen. In addition, the carbon that was picked up at the surface of the specimen did not diffuse into the metal, but remained on the surface as a layer of cementite. The structure of the carbon remaining in the vicinity of the concentration of sulphide particles was coarser than that of the carbon in the centre of the specimen and was unlike the normal pearlite structure ; this structure was visible after 2 hr. at the treatment temperature. This effect appeared most clearly between about 1100° and 1200° C. and diminished as the temperature was raised further.

These experiments indicate that even with a very high carbon content, sulphur is slightly soluble and that the solubility increases with temperature ; the presence of the sulphur in solution causes the carbon to move away from the region high in sulphur and prevents carbon diffusing into the specimen from the surface. Above 1300° C. the austenite can contain a larger amount of carbon and sulphur in solution and the sulphur does not then exert such a marked effect on the carbon.

Carbon Steel in Nitrogen

Specimens of steel *A* were heated at temperatures between 1000–1300° C., in neutral atmospheres of pure dry nitrogen for periods varying between 2 and 10 hr. Treatment at 1000° C. produced very little effect but with very slow cooling from the treatment temperature a difference in spacing of the pearlite became apparent ; coarse pearlite was observed in the region of the sulphide particles, whilst much finer, more normal pearlite was observed in the regions where there were no sulphide particles. When specimens were treated at 1100° C., carbon moved away from the region of the sulphide particles towards the centre of the specimen, leaving the outer rim low in carbon, as shown in Fig. 5. The sulphide particles were generally surrounded by carbon-free zones. This movement of carbon was fairly rapid, and treatment for 10 hr. was sufficient to remove most of the carbon from the zone high in sulphur. The boundary between the outer zone containing the sulphide particles and the main portion of the steel was now clearly marked by a sudden change in carbon content. The small amount of carbon remaining in the outer zone appeared either as cementite or as very divorced pearlite. Quenching from the temperature of treatment showed that the movement of carbon occurs during the heating time and not during cooling.

Increasing the temperature to 1200° C., and then to 1300° C., produced an increase in the rate at which carbon moved away from the sulphide particles ; 2 hr. at 1300° C. were sufficient for the carbon to move away from the outer zone. At 1200° and 1300° C. there was a considerable movement of sulphur, which appeared as a fine dispersion of manganese sulphide particles. A very marked change took place on heating to 1350° C. ; the sulphur went into solution very readily and penetrated throughout the specimen, tending to concentrate around grain boundaries, as shown in Fig. 6. Very high magnification showed that, immediately surrounding the larger particles of manganese sulphide, there was a concentration of extremely small sulphide particles (*see* Fig. 7). These particles were more evident at high carbon concentrations, and the grain-boundary areas containing the large sulphide particles also showed this concentration of very small particles.

It appears that sulphur can enter into solution in iron of this particular composition. It starts to go into solution at about 1000° C. and the amount going into solution increases as the temperature increases. Carbon in solution appears to influence the amount of sulphur that can be taken into solution, particularly at the lower temperatures, but the sulphur going into solution causes the carbon to move away. There is a sudden increase in solubility at about 1350° C. and at this temperature carbon does not seem to have such a marked effect on the solubility of sulphur. High concentrations of carbon can cause sulphur to move, but with a high concentration of sulphur carbon can be forced to move from regions high in sulphur. Thus, the relative amounts of carbon and sulphur present in the iron are of considerable importance.

Free-Cutting Steel in Nitrogen

A series of experiments was carried out on free-cutting steel in nitrogen to assess the relative effects of carbon and sulphur.

The analysis of the steel used (steel *B*) was as follows : 0·14% C, trace Si, 1·02% Mn, 0·226% S, 0·056% P. It contained a high initial concentration of manganese sulphide particles ; the carbon content was relatively low. It is believed that the presence of manganese increases the solubility of sulphur. The characteristic elongated shape of manganese sulphide particles made it easy to detect any change in these particles. A second series of tests was carried out on this free-cutting steel, carburized to various carbon contents in carbon monoxide. Specimens containing carbon varying from 0·1 to 0·7% C were thus obtained and they were heated to temperatures within the range 1000–1400° C. in pure dry nitrogen ; heating times of up to 100 hr. were employed.

Low Carbon Content—The results obtained with the 0·14% C free-cutting steel confirmed many of the results obtained in the previous experiments. At the lower temperatures about 50 hr. were necessary before any effect was noticed ; after 50 hr. at 1050° C. there was a slight tendency to grain-boundary formation of pearlite. The distribution of the pearlite after 50 hr. treatment at 1100° C. can be seen in Fig. 8. This effect was accentuated on raising the temperature to 1200° C., when the pearlite became very coarse, finally tending to massive cementite around the grain boundaries (*see* Fig. 9) ; the majority of the carbon appeared as cementite after 50 hr. at this temperature. Throughout the specimen, and particularly around the large sulphide particles, dispersions of very small

Fig. 1—Nickel coated with FeS treated in CO for 50 hr. at 1000° C. Etched in 1 : 1 nitric-acetic acid × 160

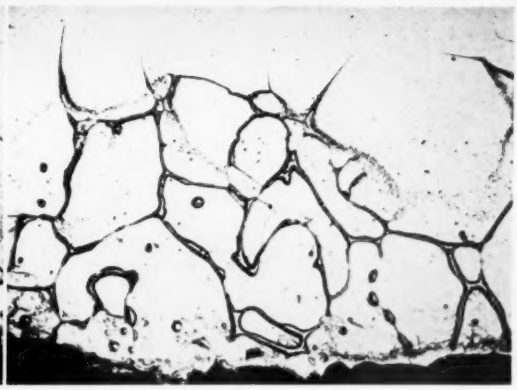


Fig. 2—Nickel coated with FeS treated in N_2 for 50 hr. at 1000° C. Unetched × 75

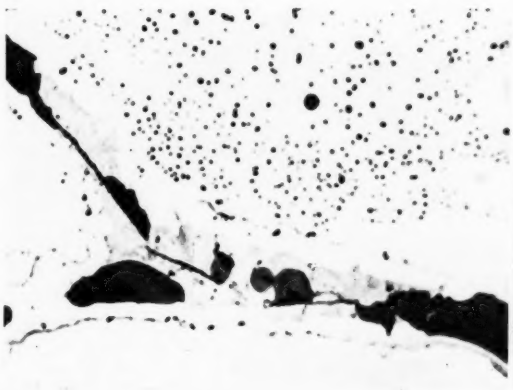


Fig. 3—Monel metal coated with FeS treated in N_2 for 50 hr. at 1000° C., showing grain-boundary region with copper sulphide and nickel sulphide surrounded by local area of nickel × 320

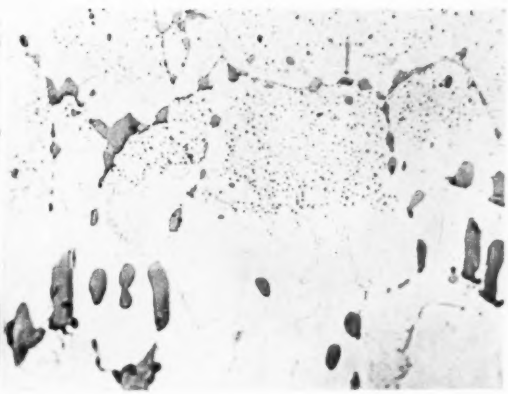


Fig. 4—Penetration of sulphide obtained in iron containing 1·5% of Mn coated with FeS and treated in CO at 1000° C., showing fine dispersion of sulphide particles × 300

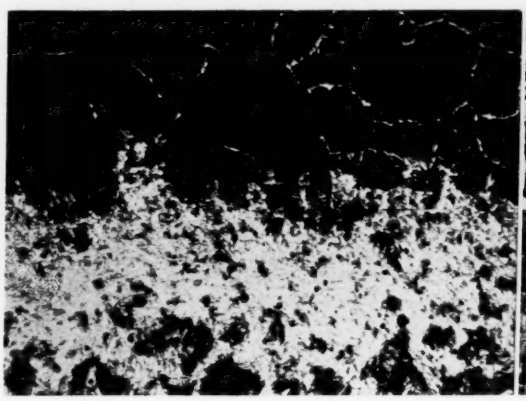


Fig. 5—Low carbon content in vicinity of high-sulphur region after treatment in N_2 for 10 hr. at 1100° C. × 140

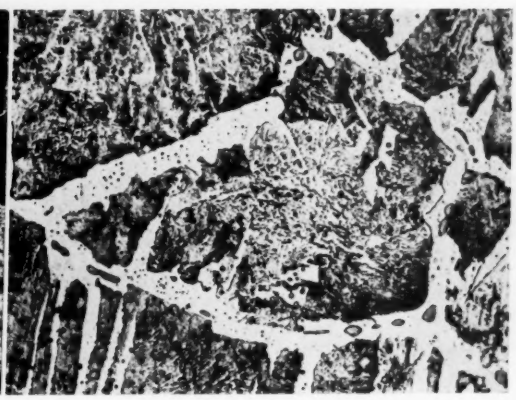


Fig. 6—Sulphide particles around grain boundaries after treatment in N_2 for 2 hr. at 1350° C. × 75

[*Irvine*

[*To face p.* 144

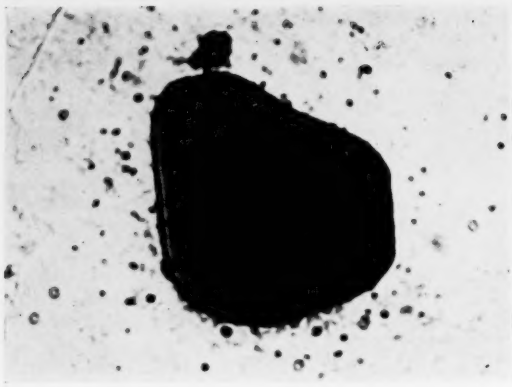


Fig. 7—Small precipitated sulphide dispersion around large sulphide particle, after treatment in N_2 for 2 hr. at 1350° C. × 1350

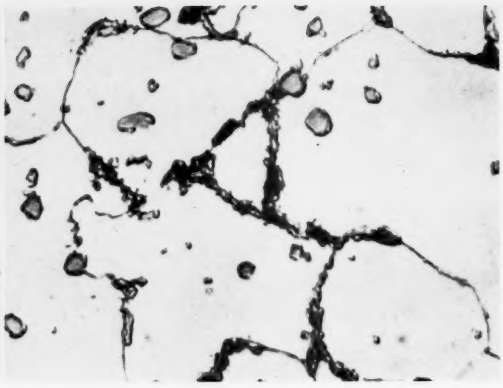


Fig. 8—Pearlite forming around grain boundaries in free-cutting steel after heating for 50 hr. at 1100° C. in N_2 × 900

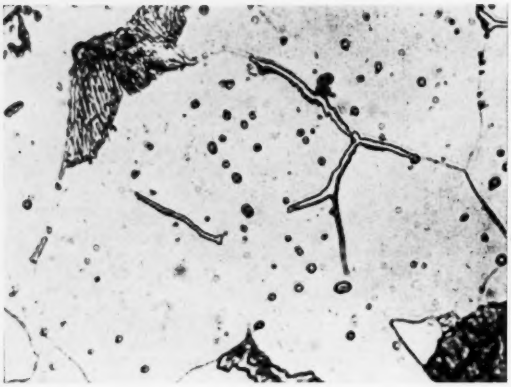


Fig. 9—Formation of grain-boundary cementite at 1200° C. × 600

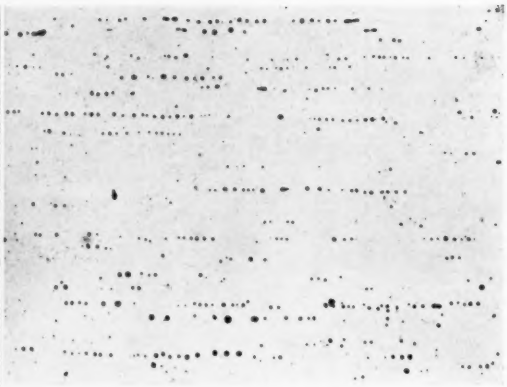


Fig. 10—Globular sulphide particles obtained after heating at 1350° C. × 75

Fig. 11—First appearance of grain-boundary sulphide precipitation after ½ hr. at 1300° C. Quenched from temperature × 1200

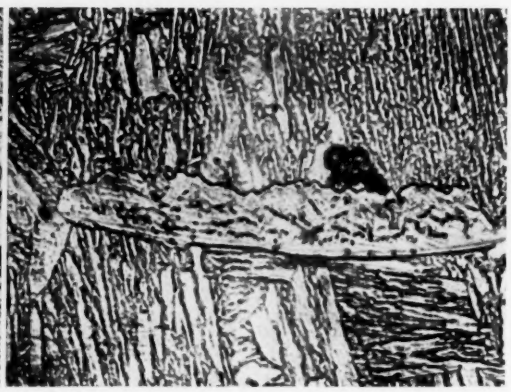


Fig. 12—Larger amount of grain-boundary sulphide precipitation after 1 hr. at 1300° C. Quenched from temperature × 1200

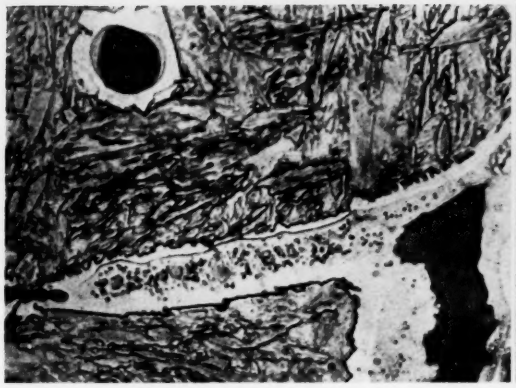


Fig. 13—Grain-boundary sulphide precipitation after ½ hr. at 1350° C.; also shows ferrite envelope forming around isolated sulphide globule. Quenched from temperature × 1200

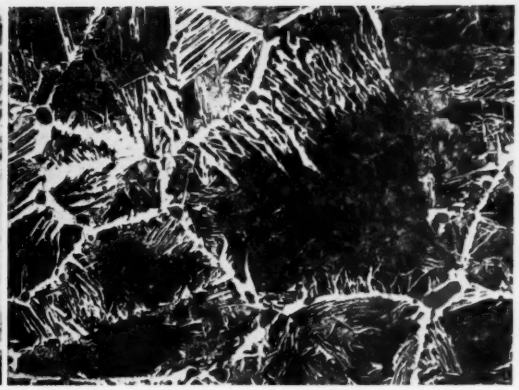


Fig. 14—Free-cutting steel carburized to 0·7% of C, heated at 1350° C. Sulphide forced to the grain boundaries × 200

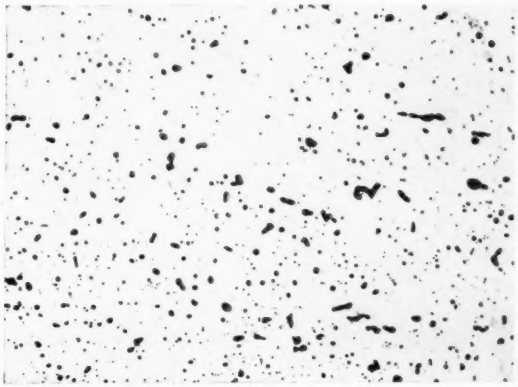


Fig. 15—Specimen as in Fig. 14 showing movement of sulphide particles to grain boundaries × 75

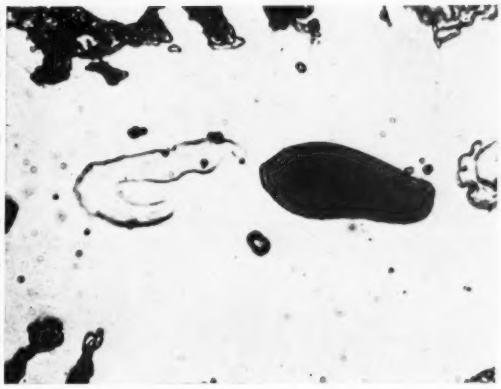


Fig. 16—Manganese sulphide particles dissolving at 1350° C. to form separate phase × 1350

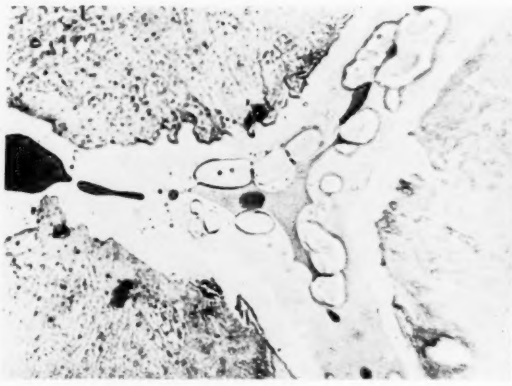


Fig. 17—Iron sulphide forming at grain boundaries at 1400° C. × 1350

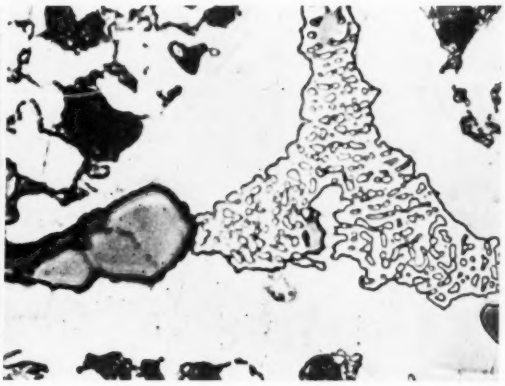


Fig. 18—Elimination of grain-boundary phase high in sulphur by heat-treatment at 900° C. × 1350

[*Irvine*

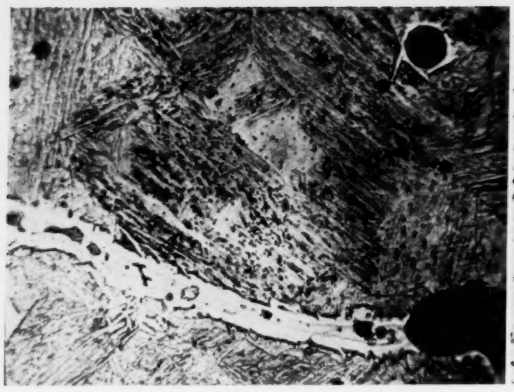


Fig. 19—Concentration of sulphide particles obtained in region high in carbon after heating to 1350° C. Quenched from temperature. Etched in nital × 1200

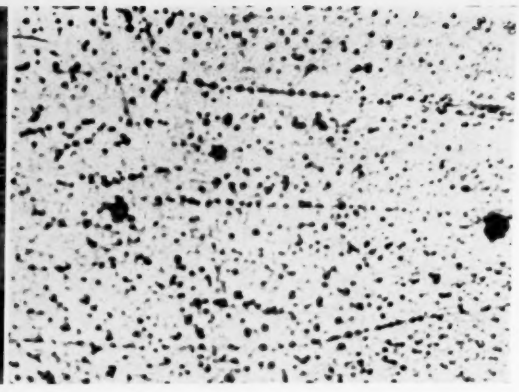


Fig. 20—Sulphide particles similar to those in Fig. 19 showing more pronounced structure. Unetched × 2000

Fig. 21—Grain-boundary sulphides obtained after heating above solidus, showing that carbon has re-entered grain-boundary region × 300

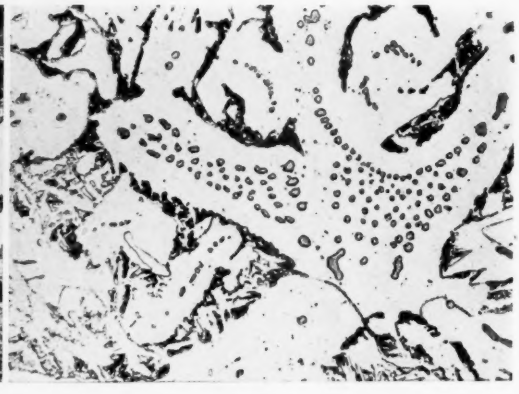


Fig. 22—Structure of free-cutting steel after melting, showing similarity to Fig. 21 × 300

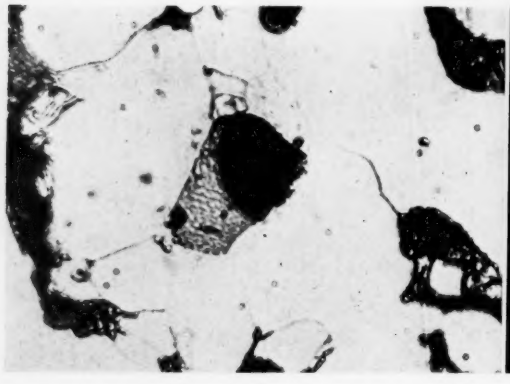


Fig. 23—Eutectic associated with sulphide particles, after high-temperature heating × 900

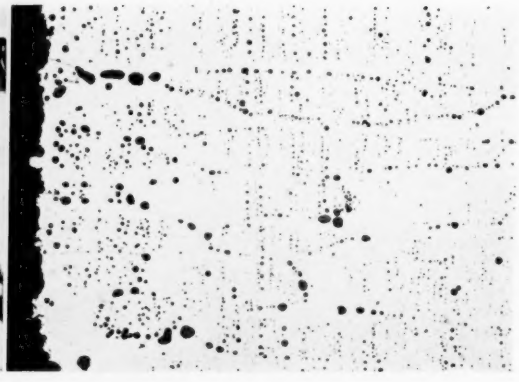


Fig. 24—Free-cutting steel heated in air for 1 hr. at 1300° C., showing molten sulphide particles along grain boundaries × 100

sulphide particles became visible ; this became more pronounced at 1300° C. As the temperature increased, the time required for these changes to take place decreased. A period of 20 hr. at 1300° C. produced more evidence of these small sulphide particles than did much longer periods at lower temperatures. As the temperature of treatment was increased above 1250° C., the tendency for the sulphur that was going into solution to force the carbon to the grain boundaries decreased. Above 1300° C. small sulphide particles appeared at the grain boundaries, and at about 1350° C. the particles of manganese sulphide melted and became more globular, as shown in Fig. 10. At 1400° C. there was a considerable decrease in the number of large sulphide particles, and the sulphur appeared to have gone into solution.

These experiments confirm that at about 1050° C. sulphur starts to go into solution and displaces carbon from solution in the austenite. This carbon moved to the grain boundaries ; on cooling, the normal pearlite transformation was not possible and cementite was formed. This effect of sulphur on the carbon was at a maximum between 1150° and 1200° C. The rate at which sulphur entered solution was slow at the lower temperatures and showed a marked increase at about 1350° C. Above about 1350° C. the carbon in solution appeared to exert the greater effect and sulphur was displaced to the grain boundaries.

Higher Carbon Content—Several important differences were noticed when more highly carburized free-cutting steel was used. At temperatures between 1000° and 1200° C. there were some slight alterations in the structure of the pearlite (with a tendency for cementite to appear) in the specimens carburized to about 0·3–0·4% C, whereas with the higher carbon contents little effect was visible. Above 1200° C. there were four stages in the development of the structure. The first was the appearance of small precipitated sulphide particles at the grain boundaries ; the exact temperature of formation depended upon the carbon content, and varied from 1200° C. for the 0·6–0·7% C to 1300° C. for the 0·14% C specimen. The latter temperature coincided with a change in carbon distribution, and quenched specimens were examined. Figure 11 shows the grain-boundary sulphide, which became visible after about ½ hr. at 1300° C. in the 0·14% C specimen. The amount of this sulphide increased with longer treatment times and at higher temperatures (*see* Figs. 12 and 13).

At 1350° C. the second stage occurred ; rapid movement of sulphur took place, and the larger sulphide particles, which at this temperature appeared to have melted, also moved to take up a position around the grain boundaries. This movement depended upon the carbon content. With 0·14% C the distribution of large sulphide particles was not appreciably changed, but with 0·4% and higher carbon contents, the sulphide particles were forced to the grain boundaries (*see* Fig. 14). Figures 15 and 10, showing specimens with 0·7% C and 0·14% C respectively, demonstrate the effect of carbon. Figure 13 also shows that where isolated sulphide particles occur within the grains, carbon moves away to leave a ferrite envelope surrounding the particles. This movement of sulphur was rapid ; ½ hr. at 1350° C. was sufficient to produce the structure shown in Fig. 14.

At 1350° C. the large sulphide globules dissolved completely leaving a distinct phase visible under the microscope, as shown in Fig. 16. The amount of this phase depended on the time of treatment and the temperature.

The third stage occurred at 1400° C. when iron sulphide began to be visible within this grain-boundary phase. The iron sulphide was sometimes associated with manganese sulphide, possibly because excess sulphur was forced to the grain boundaries and exceeded the local supply of manganese necessary to form manganese sulphide (*see* Fig. 17). This structure can be compared with that of Monel metal (*see* Fig. 3). With Monel metal, when the local supply of copper was exhausted, nickel sulphide started to form. Another explanation of the formation of sulphide particles at these temperatures is that the grain-boundary region has been completely depleted of carbon, and in carbon-free material the $\gamma \rightarrow \delta$ change might be expected to occur at this temperature. If the δ-phase has a smaller solubility for sulphur the latter would be precipitated.

When the manganese sulphide particles dissolved at 1350° C. the separate phase shown in several of the photographs was always formed. This phase was very high in sulphur and always showed a definite boundary with the normal ferrite. The high sulphur content was shown by treating the specimens, in which this phase had been produced, at 900° C. At this temperature, carbon migrated to the grain-boundary area. The amount of this phase gradually decreased and manganese sulphide was formed ; this manganese sulphide remained around the grain boundaries when the phase had entirely disappeared. Figure 18 shows a stage in the elimination of this phase. Above 1350° C., the sulphur readily diffused through the body of the metal, even if the metal had a high carbon content. Figure 19 shows an example of a large concentration of sulphide particles within the area high in carbon, and Fig. 20 shows another example quenched from 1400° C. The structure of these sulphide particles is more pronounced and is similar to that described by Wheeler, Kondic, and Ko.[2]

As far as could be judged, except in the specimens containing more than 0·7% of C, the solidus had not been exceeded by heating to 1400° C. However, when the temperature was raised above 1400° C., definite grain-boundary melting took place and the sulphide assumed the characteristic form shown in Fig. 21. When this fourth stage occurred, the carbon re-entered the grain-boundary region, and the structure was in many respects similar to that obtained in free-cutting steel that had been intentionally heated above the solidus, as shown in Fig. 22. An abrupt change took place as the grain-boundary melting occurred, and there was no possibility of confusing this new distribution of sulphide particles with that existing at temperatures just below the melting point.

Melting of Large Sulphide Particles

Experiments to determine the temperature at which the large sulphide particles melted and entered solution showed that they occasionally melted at a lower

XUM

temperature than was expected. In such cases the particles formed a eutectic, which appeared to have iron sulphide as one of its constituent parts (*see* Fig. 23). This type of constituent had been previously observed near the surface of free-cutting steel heated at a high temperature in an atmosphere of nitrogen containing 2% of oxygen. The principal effect of oxygen was to cause the sulphide particles in the free-cutting steel to form a low-melting-point eutectic mixture. The molten particles were observed at temperatures as low as 1000° C., although increasing temperature increased the depth of penetration of the oxygen into the metal. In a high oxygen content, *i.e.*, in air, the particles appeared to contain manganese sulphide associated with the oxide, whereas with the low oxygen content of the prepared atmospheres, iron sulphide was present. The unexpectedly low melting point of some manganese sulphide particles to form a eutectic containing iron sulphide may have been caused by the oxygen in solution in the metal enabling the iron sulphide–iron oxide eutectic mixture to form.

The experiments carried out in air showed that, although an ample supply of oxygen at the surface caused the sulphide particles to melt at temperatures considerably below 1200° C., the sulphide particles near the surface did not enter solution even when the temperature was raised above that at which manganese sulphide particles were melting and entering solution in the centre of the specimen. Therefore, a high concentration of oxygen in solution in iron effectively prevents sulphur going into solution. On the other hand, the small amount of oxygen normally present in steel may increase the tendency for sulphur to dissolve as it lowers the temperature at which the manganese sulphide particles melt, without giving a sufficiently high concentration of oxygen in the steel to prevent sulphur from dissolving.

The very marked effect that oxygen has in causing the sulphide particles to melt at a lower temperature than usual is shown in Fig. 24, which shows the microstructure of a specimen heated for 1 hr. at 1300° C. Away from the edge of the specimen, the elongated particles of manganese sulphide are arranged in the direction of rolling, whereas at the edge of the specimen the molten sulphide–oxide eutectic particles have been completely rearranged along the long columnar grain boundaries which have been formed. These particles showed no tendency to go into solution, even when the temperature was raised to a point at which the sulphide particles in the centre of the specimen dissolved rapidly. In contrast, oxide–sulphide particles produced near the surface of the specimen by an atmosphere containing only 2% of oxygen dissolved readily when the temperature was raised above 1350° C.

CONCLUSIONS

The following conclusions can be drawn from the results of experiments described in this paper :

(1) Sulphur appears to have a negligible solubility in pure iron, but when manganese or nickel are present in small amounts in the iron, sulphur is appreciably soluble, the solubility increasing rapidly with temperature. Sulphur appears to enter solution at temperatures from 1000° C. upwards, but the rate of solution is very slow until about 1300° C.

(2) In iron containing these additions there is a rapid increase in solubility at about 1350° C., and in the rate of solution, probably because the sulphide particles melt.

(3) Oxygen in solution in the iron appears to lower the temperature at which the sulphide particles melt.

(4) The ratio of carbon to sulphur in the iron determines which element will exert the most powerful effect and so displace the other. With the typical sulphur content of free-cutting steel, the balancing carbon content changes from about 0·3% at 1150° C. to less than 0·14% at 1300° C. With the lower carbon contents, carbon is displaced to the austenite grain boundaries, whereas with higher carbon contents, sulphur is forced to the grain boundaries. With the much lower sulphur contents of commercial steels, carbon will in all cases cause movement of sulphur to the grain boundaries.

(5) At temperatures above the melting point of the sulphide particles, sulphur rapidly enters solution, forming a metallographically distinct phase round the grain boundaries.

(6) At about 1400° C. iron sulphide forms at the grain boundaries within the sulphur-rich phase.

Comparison with Earlier Results

These results cannot be directly compared with those of other workers because the composition of the materials used differs considerably. However, the experiments were intended to amplify conclusions previously reached. Accounts of previous work are given in the Symposium on Overheating,[3] and in further papers by Preece, Nutting, and Hartley,[4] and Wheeler, Kondic, and Ko.[2] The earlier work is summarized by Ko and Hanson,[5] who, by developing a technique for the examination of fractured surfaces, were able to demonstrate that manganese sulphide particles were precipitating at the grain boundaries. The work of the present author substantiates these results, and in some respects enlarges upon them. Ko and Hanson classified in three stages the changes taking place. In their first stage manganese sulphide particles appeared at the grain boundaries at relatively low temperatures, *e.g.*, at 1150° C. in a 0·85% C steel, and this has been confirmed. Their second stage was the precipitation of sufficient manganese sulphide particles to cause the overheated structure visible by etching with nitro-sulphuric acid. The lowest temperature they quoted was 1300° C., which corresponds reasonably closely with the first appearance of significant amounts of manganese sulphide at the grain boundaries in the experiments described in this paper. Their third stage comprised several changes, including the formation of an iron-rich sulphide and visible segregation of impurities to grain-boundary regions because the temperature exceeded the solidus. Not all the changes taking place could be explained by assuming the metal to enter the solidus–liquidus range. Further work is necessary on the effect of phosphorus, and on the effect on the melting point of the sulphide particles of oxygen in solution. The possibility of the $\gamma \rightarrow \delta$ change taking place in the low carbon regions at the grain boundaries must be

considered. The marked difference between these changes and the precipitation of manganese sulphide particles at the grain boundaries which produces 'overheating' and seriously affects the mechanical properties, justifies the description 'burning.'

The changes taking place during overheating involve the diffusion of sulphur, and it has been shown that this occurs at temperatures as low as 1000° C., although at this temperature the solubility is low and the rate of diffusion is slow. Nevertheless, the time factor must be stressed when considering to what extent diffusion will take place during industrial heat-treatment processes. Too little attention has been paid to other factors affecting the solubility of sulphur, particularly the composition of the iron, and the relative amounts of carbon and sulphur present in the steel. The indications are that sulphur is in interstitial solution in austenite, in which case it will be the relative effect of carbon and sulphur that is important; sulphur will be expected to exert a greater effect when the carbon is high than when it is low.

Industrial Implications

Many of the results described have important industrial implications. This is not because iron sulphide will enter steel under the influence of carburizing conditions, although the particular case of peel formation on malleable cast iron has previously been described.[6] There are, however, many instances where a heterogeneous ferrous alloy has local concentrations of carbon and sulphur, and if this metal is subjected to high temperature then the resulting movement of carbon or sulphur may produce a profound change in mechanical properties. When a heterogeneous metal is subjected to high-temperature heat-treatment, diffusion changes usually remove the heterogeneity, but with carbon and sulphur the tendency is for this heterogeneity to increase within the temperature limits which cause sulphur to go into solution, *i.e.*, 1000–1300° C. At the upper limit sulphur does not exert such a marked effect on the movement of carbon. This may explain the disappointing results obtained in experimental work on the high-temperature heat-treatment of steel castings. Wheeler, Kondic, and Ko[2] have discussed the changes taking place in areas adjacent to welds, and the subject has recently been attracting the attention of other workers. Thus, the related diffusions encountered with carbon and sulphur are of interest from many points of view during high-temperature heating of steel.

References

1. A. Preece and K. J. Irvine : *J. Iron Steel Inst.* 1947, vol. 157, pp. 336–343.
2. J. A. Wheeler, V. Kondic, and T. Ko : *Ibid.*, 1951, vol. 167, pp. 301–308.
3. "Symposium on Overheating," *Ibid.*, 1946, No. I, pp. 217P–317P.
4. A. Preece, J. Nutting, and A. Hartley : *Ibid.*, 1950, vol. 164, pp. 37–45.
5. T. Ko and D. Hanson : *Ibid.*, 1950, vol. 164, pp. 51–62.
6. A. Preece and K. J. Irvine : *Ibid.*, 1948, vol. 158, pp. 3–8.

Addition of Boron to Steel by Reduction from Boron Oxide

By G. E. Speight, B.Sc., F.R.I.C., F.I.M.

SYNOPSIS

Previous work on the boron–oxygen equilibrium in liquid iron and evidence of boron pick-up from the fortuitous presence of borates in high-frequency and arc furnace linings had suggested the possibility of adding boron to steel by reduction from a slag containing boric oxide. This method has been investigated as an alternative to the commercial boron addition alloys in a series of laboratory experiments and it has been shown that boron can be introduced into steel from a borate and that the boron so added can be made effective in providing improved mechanical properties of boron steels. These properties can be achieved only by having the correct amount of boron present in the correct mode of occurrence, and the means adopted and the underlying chemical theory for ensuring the desirable occurrence of the boron are described. The laboratory techniques have yet to be applied on a commercial scale but practical recommendations for the addition of boron by this method in various steelmaking practices are outlined.

The use of boron in steel is rapidly increasing and, with it, interest in methods of adding the requisite amount of boron. Ferro-boron and other boron alloys, supplemented by heavy additions of Al and other degasifying agents, can be used successfully, and complex boron-containing deoxidation alloys, *e.g.*, Silcaz, Carbortam, are commercially available for this purpose.

The possibility of adding boron by reduction from a slag containing boric oxide has therefore been investigated as this might provide a reasonable alternative to the commercial boron addition alloys.

Manuscript received 28th March, 1952.

Mr. Speight is Chief Chemist at The United Steel Companies, Ltd., Research and Development Department, Rotherham.

Table I
ANALYSES OF HOWLITE-TREATED ELECTRIC ARC CASTS

Cast	Quality	Pit Analysis, %						Boron Determinations, %								
								Bath Sample (Before Howlite)			Pit Sample			Billet (Middle of 1st Ingot)		
		C	Mn	Si	Ni	Cr	Mo	Sol. B	Insol. B	Total B	Sol. B	Insol. B	Total B	Sol. B	Insol. B	Total B
Howlite Treatment: None																
H6127	En 22	0·43	0·54	0·22	3·45	0·20	...	...	...	...	...	...	...	...	...	...
H6128	,,	0·42	0·55	0·24	3·48	0·13	...	...	...	...	...	...	...	...	...	...
H6129	En 36	0·10	0·45	0·22	3·16	0·82	...	...	...	...	...	...	...	...	...	...
H6130	,,	0·13	0·43	0·23	3·16	0·89	...	...	...	...	...	...	...	Nil	Nil	Nil
H6131	,,	0·11	0·45	0·24	3·25	0·95	...	...	...	...	...	...	...	...	...	...
H6132	En 24	0·37	0·60	0·22	1·52	1·05	0·28	...	...	...	...	...	...	Nil	Nil	Nil
Howlite Treatment: 18 lb.																
H6133	En 24	0·40	0·60	0·25	1·45	1·06	0·23	Nil	Nil	Nil	0·0006	0·0011	0·0017	0·0007	0·0010	0·0017
H6134	En 40B	0·27	0·53	0·28	0·25	3·20	0·55	...	...	...	...	...	...	...	...	...
H6135	En 36	0·16	0·48	0·21	3·19	0·93	...	Nil	Nil	Nil	0·0906	0·0010	0·0016	0·0005	0·0010	0·0015
Howlite Treatment: 36 lb.																
H6136	En 36	0·13	0·42	0·21	3·34	0·88	...	Nil	Nil	Nil	0·0008	0·0016	0·0024	0·0007	0·0016	0·0023
H6137	En 24	0·34	0·59	0·22	1·54	1·06	0·27	0·0002	Nil	0·0002	0·0014	0·0017	0·0031	0·0011	0·0018	0·0029
H6138	,,	0·39	0·56	0·24	1·53	1·06	0·27	0·0001	Nil	0·0001	0·0007	0·0016	0·0023	0·0006	0·0017	0·0023
H6139	...	0·18	0·52	0·24	0·24	1·08	...	...	...	...	...	...	...	...	...	...

The work of Derge[1] on the boron–oxygen equilibrium in liquid iron indicated the feasibility of this method, and the author's experience of boron pick-up from the fortuitous presence of borates in high-frequency and arc furnace linings supported this view.

To study whether the use of boron oxide could be controlled sufficiently for commercial purposes, a series of laboratory experiments has been carried out. These experiments show that boron can be introduced into steel from a borate, and that the boron so added can improve the mechanical properties of boron steels.

The induction-furnace and laboratory trials described later in this paper deal with the effect of boron on a 0·08–0·12% C, 0·5% Mo steel (Fortiweld[2]), which in the normalized condition has high tensile and proof stress. This is achieved only by having the correct amount of boron present in the correct mode of occurrence ; the paper deals, therefore, with the means adopted, and the underlying chemical theory, for ensuring the correct occurrence of the boron. It is believed that there is a similar background to the boron effect in steels for improved depth hardenability.

BORON PICK-UP IN ELECTRIC ARC FURNACE PRACTICE

Effect of Howlite Additions to Electric Arc Furnace Slags

For several years it has been customary, in the basic arc furnace practice at Messrs. S. Fox and Co., Ltd. (Stocksbridge, Sheffield), immediately before shut-down periods, to treat the final (' white falling ') slag and hearth with Howlite (hydrated calcium silico-borate, $4CaO.2SiO_2.5B_2O_3.5H_2O$). This stabilizes the banks and hearth, thereby preventing deterioration during the shut-down period. The Howlite addition (36 lb. to a slag bulk of about 10 cwt., giving about 0·7% of boric oxide in the final slag) is made to the last three or four casts before shut-down. The furnace operators believed that this slag treatment had some effect on the resulting steel and it was suspected that boron was inadvertently introduced to the bath. A few preliminary tests confirmed that transfer of boron to the metal did, in fact, occur.

To obtain more detailed confirmation of this effect, the last 13 casts before the shut-down of a 10-ton arc furnace were studied as follows :

(*a*) To the first six casts no Howlite addition was made

(*b*) The next three casts were treated with 18 lb. of Howlite 10 min. before tapping

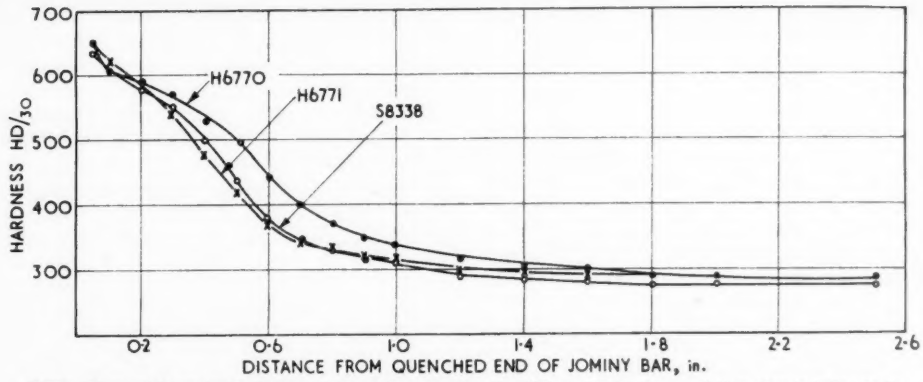
(*c*) The last four casts before shut-down were treated with 36 lb. of Howlite 10 min. before tapping.

Table II
ELECTRIC ARC HEATS TREATED WITH HOWLITE AND ALUMINIUM

Treatment

Cast S8338: 8 oz. of Al per ton to furnace; 8 oz. of Al per ton to ladle; no Howlite
Cast H6770: 16 oz. of Al per ton to furnace, followed by 48 lb. of Howlite; no Al to ladle
Cast H6771: No Al to bath; 48 lb. of Howlite to bath; 16 oz. of Al per ton to ladle

	Boron Contents, %		
	Cast S8338	Cast H6770	Cast H6771
Bath Sample before Al			
Sol.	0·0001	0·0001	0·0003
Insol.	0·0001	0·0001	0·0001
Total	0·0002	0·0002	0·0004
Bath Sample after Al, before Howlite			
Sol.	0·0001	0·0001	...
Insol.	Nil	0·0002	...
Total	0·0001	0·0003	...
Bath Sample after Howlite			
Sol.	...	0·0003	0·0002
Insol.	...	0·0024	0·0004
Total	...	0·0027	0·0006
Pit Sample			
Sol.	0·0001	0·0004	0·0003
Insol.	Nil	0·0020	0·0007
Total	0·0001	0·0024	0·0010
Billet Material (Mean)			
Sol.	0·0001	0·0003	0·0003
Insol.	0·0001	0·0022	0·0008
Total	0·0002	0·0025	0·0011



*H*6770—16 oz. of Al per ton to furnace; 48 lb. of Howlite after Al addition; *H*6771—16 oz. of Al per ton to ladle; 48 lb. of Howlite to furnace; S8338—8 oz. of Al per ton to furnace; 8 oz. of Al per ton to ladle; no Howlite added

Fig. 1—Jominy hardenability tests on Howlite-treated arc furnace casts

Furnace samples, pit samples, and billet samples were taken from these heats and examined for boron content. Both 'acid-soluble' and 'acid-insoluble' boron determinations[3, 4] were made; their relative significance is discussed later. The results and the general pit-sample analyses are given in Table I.

This examination showed clearly that boron may be introduced into electric arc steels by adding a borate to the refining slag shortly before tapping. Whilst the amount of boron so introduced into the steel is doubtless dependent on slag composition, state of oxidation, and temperature of the bath, there was a remarkably close correlation between the borate addition to the slag and the boron found in the steel. Thus, 18 lb. of Howlite added to the slag gave boron contents of about 0·0015% in the steel, whilst twice the weight of Howlite, 36 lb., gave boron contents between 0·0023 and 0·0029%.

Believing the efficiency of boron transfer and its metallurgical effectiveness to be affected by the intensity of deoxidation, a series of arc furnace casts of 0·35% C, 1·5% Mn, 0·25% Mo quality was studied, in which the effect of Al additions before and after the borate treatment was examined. Because of specification limitations the amount of Al added had to be limited to that used for normal deoxidation and grain-size control for this quality.

The boron contents of bath, pit, and billet samples from these casts are recorded in Table II. The results for casts *H*6770 and *H*6771 show that deoxidation with Al before the borate addition to the slag substantially improved the yield of boron to the metal. However, end-quench hardenability tests on billets from these casts (Fig. 1) revealed no significant benefit from the boron. This was surprising as cast *H*6770 at least had a boron content (0·0025%) which, according to information then available, should have produced an effect on depth hardenability. However, the boron occurs substantially in the 'acid-insoluble' form and the amount of 'acid-soluble' boron is relatively small. Subsequent work[5] has shown that this acid-insoluble form can be suppressed by additions of Ti or Zr, ensuring that the boron present shall be substantially as acid-soluble, which is the effective form. Thus, had it been permissible to make a small addition of Ti, cast *H*6770 would have responded to the boron treatment.

Boron Pick-up from Induction Furnace Linings

The incidental pick-up of boron from induction furnace linings was suspected from the examination of samples from 2-ton induction furnace heats of boron-treated 0·5% Mo steel (Fortiweld). The boron contained in these heats was substantially higher than that added as Silcaz. The typical results in Table III indicate a boron pick-up of about 0·001–0·002%. The induction furnace lining, consisting of sea-water magnesia with 4% of sand and 2% of borax, appeared to be the source of the extraneous boron.

Samples of other induction furnace qualities were examined to see whether this adventitious boron was a general feature of all induction furnace heats in

Table III

BORON ANALYSES OF TWO 2-TON INDUCTION FURNACE CASTS OF FORTIWELD

Cast	Boron, %, Added as Silcaz	Sample	Boron, %		
			Sol.	Insol.	Total
DB9772	0·004	Pit	0·0052	0·0001	0·0053
		Billet 1	0·0046	Nil	0·0046
		Billet 2	0·0051	Nil	0·0051
C1615	Nil	Bath	0·0009	0·0001	0·0010
	0·004	Pit	0·0061	Nil	0·0061

Table IV

BORON ANALYSES ON COMMERCIAL INDUCTION FURNACE CASTS (Pit Samples)

Cast	Age of Lining	Boron, %		
		Sol.	Insol.	Total
C1559	9th heat	Nil	Nil	Nil
C1694	5th heat	0·0002	Nil	0·0002
C1696	7th heat	0·0003	Nil	0·0003
A17831	81st heat	0·0002	0·0001	0·0003

such linings. Whilst the results (Table IV) show some evidence of boron pick-up, it is by no means so great as that found in the boron-treated casts, nor was there any clear indication that the age of the lining affected the amount of boron pick-up.

The next commercial heat of boron-treated steel was examined in greater detail to determine whether the boron picked up from the lining could be made metallurgically effective. This was a commercial 2-ton high-frequency heat of Fortiweld[2] (*F*3461) to which Silcaz, equivalent to 0·0035% of boron, was added. Before the Silcaz addition, however, a small hand-shank of the metal was taken and treated with a smaller Silcaz addition, equivalent to only 0·001% of boron, and then cast into an 18-lb. test ingot. The purpose of this test ingot was to determine whether the small addition of boron, 0·001%, itself insufficient to give the enhanced properties of Fortiweld, might do so when added to the boron believed to be already present from the furnace lining. The boron analyses given in Table V show that, whilst the main cast contained the expected boron increment (0·0012%), the 18-lb. test ingot indicated only minor boron pick-up, 0·0002–0·0003%. The substantial boron pick-up of 0·0012% was evident only after the addition of Silcaz (and the accompanying heavy Al treatment) had been made to the metal. The mechanism of its origin may be stated as follows :

Erosion of the furnace lining produces a slag containing boric oxide which is potentially capable of reduction to the metal. The amount of boron so transferred from slag to metal will depend upon factors such as temperature, slag and metal compositions, and in particular their states of oxidation. The transfer of boron from slag to metal will be favoured by a low state of oxidation. Consequently, only those heats which are strongly deoxidized *in the presence of the borate slag*, either in the furnace or in the ladle, show the high boron pick-up of 0·001% or more. The 18-lb. test ingot showed only negligible boron pick-up because it was deoxidized in the absence of a borate slag cover.

The examination of cast *F*3461 showed that, for efficient transfer of boron from a borate slag to the metal, adequate deoxidation of the metal is essential.

Table V

BORON ANALYSES ON 2-TON HIGH-FREQUENCY CAST F3461

	Boron, % Added as Silcaz	Boron, %			
		Sol.	Insol.	Total	Pick-up
		Main Cast			
Bath sample	Nil	0·0003	Nil	0·0003	0·0003
Tapping sample	Nil	0·0003	Nil	0·0003	...
Pit sample	0·0035	0·0047	Nil	0·0047	0·0012
		18-lb. Test Ingot*			
Top	...	0·0012	Nil	0·0012	...
Middle	...	0·0013	Nil	0·0013	0·0003
Bottom	...	0·0014	Nil	0·0014	...

*0·001% B added as Silcaz

The boron so transferred, however, may not show benefit to the steel unless, as mentioned before, the nitrogen is also stabilized. This is discussed in the following section.

FACTORS CONTROLLING THE OCCURRENCE AND EFFECT OF BORON IN STEEL

Boron–Oxygen Equilibrium

Gurry[6] studied the thermodynamics of the boron–oxygen equilibrium in liquid steel and, from his calculations, concluded that the deoxidizing power of boron should be of a similar order to that of Al. Derge's later experimental study[1] of the same equilibrium indicated that the affinity of boron for oxygen was more akin to that of Si than Al. Whilst there must, therefore, remain some uncertainty regarding the precise evaluation of the boron–oxygen equilibrium, it is definitely established that boron has very considerable deoxidizing power. Consequently, before appreciable transfer of boron to metal from a borate slag can occur, the metal must be adequately deoxidized ; of the common deoxidizers (Mn, Si, Al) only Al is strong enough to lower sufficiently the oxygen potential of the metal.

Mode of Occurrence of Boron and Effect on Properties

During the early study of boron-treated steels it became apparent that boron in steel occurred in two forms, one ' soluble ' in dilute sulphuric acid and the other ' insoluble.' The proportion of the two forms present was not constant but could be varied according to the method of making the boron addition and its accompanying degasification treatment, and sometimes according to the subsequent heat-treatment of the steel. Although the ultimate form of the acid-soluble boron has not been definitely established, it is this fraction of the total boron present which modifies the transformation characteristics of the steel and gives the enhanced physical properties of boron-treated steels. This aspect of the effect of boron in 0·5% Mo steel has been discussed in detail by Bardgett and Reeve,[2] but for the present purpose the effect may be briefly explained by saying that the presence of a small amount of boron in steels of certain composition depresses the ferrite transformation at slower rates of cooling. The minimum rate of cooling, below which the transformation temperature is not depressed, has been called the Limiting Rate of Cooling (L.R.C.) and on this basis a discriminating test for boron-treated steels has been developed by the author's colleagues. Thus, for untreated low-carbon 0·5% Mo steel, the L.R.C. is greater than 180° C./min., but for the same steel after effective treatment with boron it is 20–35° C./min. The presence of at least 0·0012% of acid-soluble boron is, however, required.

The acid-insoluble boron fraction, which is without effect in this test, has been identified as boron nitride.[5] The problem, therefore, is to ensure the presence of sufficient acid-soluble boron by controlling the formation of boron nitride ; *i.e.*, the nitrogen must be stabilized by the addition of elements having a greater affinity for nitrogen than has boron ; the principal elements are Ti and Zr. Thus the success of an alloy such as Silcaz* for boron addition may be attributed

* Approximate analysis : 0·5% B, 40% Si, 10% Ca, 10% Ti, 4% Zr, 7% Al, 28% Fe.

to its high content of Ti and Zr, acting primarily, not as deoxidizers, but as nitrogen stabilizers.

Once these principles are appreciated, other boron alloys such as ferro-boron, aluminium–boron, boron-rich molybdenum silicide, etc., may be used with complete success, provided that the following conditions are satisfied :

(*a*) Complete deoxidation to avoid oxidation loss of boron and the nitrogen-stabilizing elements
(*b*) Stabilization of nitrogen by Ti and/or Zr, the amounts of which depend on the nitrogen content.

In the presence of a deoxidizer, *e.g.*, Al, and a nitrogen stabilizer, *e.g.*, Ti, boron additions to steel can be closely controlled. Recovery of the boron so added is almost substantially as effective acid-soluble boron. However, advantage can be taken of the nitrogen-stabilizing property of boron itself and the Ti addition can be omitted if necessary. Under such conditions the recovery of soluble boron is low and less controllable, and the boron addition must be increased to compensate for loss of boron due to reaction with nitrogen. When Ti is omitted it is an advantage also to increase the Al addition.

If the foregoing conditions are not satisfied, the steel, whilst having an apparently adequate acid-soluble boron content ($> 0{\cdot}0012\%$), may not show the expected properties. Such steels have not been adequately degasified. As already mentioned, the deoxidizing powers of boron and Si are similar and, also like Si, the affinity of boron for oxygen increases with decreasing temperature. Consequently, when boron is added to a steel which has been deoxidized with Si only, or with insufficient Al, boron oxide may form during the cooling and solidification processes. Boron oxide formed in this way is acid-soluble but is metallurgically inactive. It must be remembered, therefore, that high acid-soluble boron is not of itself a guarantee that the boron will be effective ; it is necessary also, by thorough Al treatment, to prevent the formation of this useless form of acid-soluble boron.

LABORATORY EXPERIMENTS WITH BORATE SLAGS AND SODIUM BORATE

Having established the conditions essential for effective boron treatment of steel, laboratory experiments were carried out to see how these principles apply to the addition of boron to steel *via* borate slags.

A laboratory spark-gap induction furnace was used and seven 8-kg. melts were made in a sillimanite crucible as follows :

The basic composition of the melts was $0{\cdot}14\%$ C, $0{\cdot}40\%$ Mn, $0{\cdot}20\%$ Si, $0{\cdot}45\%$ Mo. After melting and making the normal additions, 6 g. of Al and 12 g. of ferro-titanium were added for deoxidation and nitrogen stabilization and the melt was then covered with 160 g. of slag mixture, consisting of lime plus 1, 2, 5, 10, or 20% of borax. The initial slag-mixture/metal ratio was thus 2% but this increased by lining erosion during the treatment. After adjusting the metal temperature to 1600° C. the slag and metal were held in contact for 5 min. (the last two casts *SG*7263 and *SG*7266 were held for 10 min.). The slag was then removed and the metal was cast. The

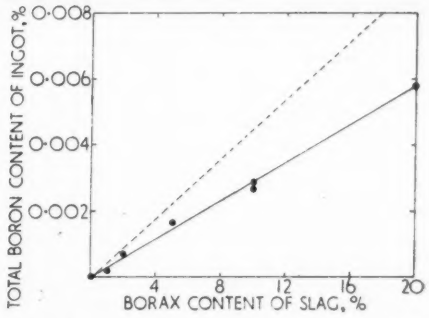


Fig. 2—Relationship between borax content of slag and resultant boron content of metal

results are recorded under the first seven casts in Table VI.

These tests showed a progressive increase in the total boron content of the ingot with increasing borax content of the slag mixture. As shown in Fig. 2, the relationship between the boron content of the steel and the borax addition to the slag was almost linear, and increasing the reaction time from 5 to 10 min. gave no significant increase in the boron content (*see SG*7213, *SG*7263, and *SG*7266).

With 10% of borax in the slag mixture the acid-soluble boron in the steel exceeded $0{\cdot}0015\%$, previously shown to be the minimum requirement to give the characteristic properties of this type of boron steel. Determination of the L.R.C., however, indicated that the ferrite transformation was not suppressed and therefore that the steel would not show the required properties. Even with 20% of borax in the slag mixture, giving $0{\cdot}003\%$ acid-soluble boron in the steel, L.R.C. determination indicated only borderline properties.

These results were rather disappointing in view of the precautions taken to deoxidize the steel and to stabilize the nitrogen before the slag treatment. However, a high proportion of the boron introduced was acid-insoluble, indicating the formation of boron nitride which should not have occurred in view of the Ti addition. This implied that the Ti had been lost by oxidation and, if so, the Al also must have been similarly oxidized. The later casts of this series were therefore examined spectrographically, and Ti and Al were almost entirely absent. The high acid-insoluble boron content was thus caused by loss of stabilizing Ti. Also the absence of Al was indicative of a residual oxygen content high enough to cause the formation of boron oxide during cooling and solidification. The acid-soluble boron fraction was likely therefore to contain a high proportion of the ineffective oxide, and this would explain the low L.R.C.

It appeared, therefore, that the Al and Ti additions before slag treatment had been nullified by oxidation during the slag treatment, and that deoxidation and nitrogen-stabilization treatments after the slag reaction period were necessary. Accordingly, the next experimental cast (*SG*7343) was made with additions of Al and ferro-titanium before and after slag treatment with a slag mixture containing 20% of borax : practically all the boron in the steel then occurred

in the acid-soluble form. L.R.C. determinations indicated that the boron would be effective and that the steel would have the desired physical properties. Furthermore, the total boron yield to the metal was increased to 0·0089%, an increase of almost 60% over the preceding cast, which had been treated identically apart from the final Ti and Al additions. Spectrographic examination confirmed the presence of residual Ti and Al sufficient to ensure complete nitrogen stabilization and deoxidation.

The conditions necessary for introducing the requisite amount of boron by reduction from a borate slag now seemed clear. Ferrotitanium before the slag treatment was unnecessary and could be omitted (the Al addition at this stage was still retained for initial deoxidation). After slag treatment the metal should be treated with Al and ferro-titanium. Taking into account the improved boron yield with this technique and again assuming a linear relationship between the borax content of the slag and the resultant boron content of the steel (giving the broken line shown in Fig. 2), it seemed that a boron content of 0·004–0·0045% could be obtained by treatment with a slag mixture con-

Table VI—LABORATORY EXPERIMENTS ON ADDITION OF BORON TO STEEL VIA BORATE SLAGS

Cast	Additions before Slag Treatment		Slag Mixture				Additions after Slag Treatment		Sample	Analysis, %													L.R.C. Assessment
	Al, g.	Fe–Ti, g.	Composition	Ratio of Slag Mixture to Metal, %	Time of Reaction, min.	Casting Temp., °C.	Al, g.	Fe–Ti, g.		C	Mn	Si	Mo	Ti	Al	Boron			Nitrogen				
																Sol.	Insol.	Total	Sol.	Insol.	Total	
SG7194	6	12	Lime	2	5	1610	...	...	Ingot	0·12	0·40	0·21	0·44			Nil	Nil	Nil	0·0048	0·0012	0·0060	
SG7195	6	12	Lime+1% borax	2	5	1610	...	...	Ingot	0·11	0·42	0·22	0·44			0·0002	Nil	0·0002				
SG7196	6	12	Lime+2% borax	2	5	1610	...	...	Ingot	0·13	0·40	0·22	0·41			0·0006	0·0001	0·0007				
SG7212	6	12	Lime+5% borax	2	5		...	...	Ingot Bar	0·15	0·44	0·18	0·43	0·01	0·01	0·0012 0·0014	0·0003 0·0004	0·0015 0·0018	0·0074 0·0084	0·0014 0·0018	0·0088 0·0102	Bad
SG7213	6	12	Lime+10% borax	2	5		...	...	Ingot Bar	0·13	0·44	0·19	0·46	0·01	0·005	0·0014 0·0012	0·0012 0·0019	0·0026 0·0031	0·0026 0·0034	0·0034 0·0026	0·0060 0·0060	Bad
SG7263	6	12	Lime+10% borax	2	10		...	...	Ingot Bar	0·15	0·38	0·17	0·43	<0·01	<0·005	0·0018 0·0019	0·0007 0·0009	0·0025 0·0028				Bad
SG7266	6	12	Lime+20% borax	2	10	1600	...	...	Ingot Bar	0·11	0·36	0·15	0·43	<0·01	<0·005	0·0030 0·0035	0·0026 0·0024	0·0056 0·0059				Borderline
SG7343	6	12	Lime+20% borax	2	10		6	12	Ingot Bar	0·11$_5$	0·45	0·23	0·43	0·04	0·02	0·0087 0·0066	0·0002 0·0005	0·0089 0·0071	0·0030	0·0040	0·0070	Good
SG7423	6	...	Lime+10% borax	2	10	1600	6	12	Ingot Bar	0·11	0·35$_5$	0·29	0·45	0·04	0·06	0·0033 0·0040	0·0008 Nil	0·0041 0·0040				Good
SG7424	6	...	Lime+10% borax	4	10	1600	6	12	Ingot Bar	0·14	0·39	0·28	0·45	0·04	0·06	0·0052 0·0050	0·0008 Nil	0·0060 0·0050				Good
SG7693	6	...	0·0625% borax	...	5	1600	6	12	Ingot	0·13	0·44	0·27	0·46	0·04$_5$	0·10	0·0044	Nil	0·0044				
SG7694	6	...	0·125% borax	...	5	1600	6	12	Ingot	0·14	0·48	0·26	0·46	0·04	0·08	0·0100	0·0002	0·0102				

taining 10% of borax. The next experimental cast (*SG*7423) was made on these suppositions and the results agreed with expectations. The boron content was as anticipated and was virtually completely soluble ; deoxidation and nitrogen stabilization were obviously satisfactory ; and L.R.C. determination indicated the required mechanical properties.

A further cast (*SG*7424) was made and given precisely similar treatment except that 4% instead of 2% of the slag mixture containing 10% of borax was used. A higher boron yield in the metal was obtained, due presumably to the higher final B_2O_3 content of the slag. Slag analyses for casts *SG*7423 and *SG*7424 are given below :

Slag Compositions after Treatment

	Cast *SG*7423	Cast *SG*7424
SiO_2, %	42·1	39·1
Al_2O_3, %	10·9	10·5
CaO, %	33·6	36·8
MgO, %	0·45	0·40
MnO, %	5·8	4·9
TiO_2, %	1·37	0·96
FeO, %	2·6	1·9
B_2O_3, %	1·24	1·56

It was not possible to determine the final slag bulks in each experiment, but under these conditions the partition of boron between slag and metal appears to be reasonably constant, *i.e.*, $(B_2O_3)/[B]$ is approximately 300. The details of casts *SG*7343, *SG*7423, and *SG*7424 are given in Table VI.

The object of the foregoing experiments was to study the conditions for introducing boron into electric arc and induction furnace melts which, before tapping, would inevitably be in contact with a slag. Provided that the recommended Al and Ti treatments are applied it should be possible to make direct use of boron oxide for adding boron to relatively slag-free melts, such as might occur on tapping and teeming. To test this view two further laboratory trials were made (*SG*7693 and *SG*7694, Table VI). After the initial Al treatment the melts were skimmed to remove slag and were then treated with 0·0625 and 0·125% respectively of dehydrated borax ($Na_2B_2O_7$). After 5 min. Al and ferro-titanium additions were made as in the previous heats and the melts were cast into ingots.

The results fully confirmed expectations. The yield of boron was high, 58 and 66% respectively, and the boron was substantially present in the effective acid-soluble form. It is clear, therefore, that where conditions are suitable, borax and presumably other available forms of boron oxide may be used successfully for the direct introduction of boron to steel melts.

PRACTICAL RECOMMENDATIONS

The techniques described have yet to be applied on a commercial scale, but there seems little doubt of their ultimate success. The likely procedures for various types of furnace are outlined below.

Basic-Lined Induction Furnaces—After the normal additions of Mn, Si, Mo, etc., the metal should be treated with 1 lb. of Al per ton to effect initial deoxidation. Then should follow the slag treatment with about 2% of a slag mixture containing 0·5% of boron added as Howlite or other commercially available borate. (Considerable latitude in the slag composition is possible ; the electric arc trials showed that boron could be reduced from high-lime slags, whilst in the laboratory trials using lime–borax mixtures the final slag was neutral in character due to lining erosion. In practice, therefore, a blast-furnace slag, an electric arc ' white-falling ' slag, or even a synthetic lime–alumina–silica mixture might each be satisfactory.) In certain cases, it should be possible to dispense entirely with the slag admixture and to make the borate addition direct through the existing slag or to the clean metal surface, but there might be less control over the amount of boron in the steel. The temperature should be adjusted to 1600° C. and 5 min. allowed for the reaction after fusing the slag mixture. Finally, the metal should be treated with 2 lb. of Al per ton and 3½–4 lb. of ferro-titanium (40%) per ton for final deoxidation and nitrogen stabilization.

Alternatively, the ferro-titanium may be omitted, in which case the Al addition should be increased.

Electric Arc Furnaces—When metal and white-slag conditions are finally adjusted shortly before tapping, the bath should be deoxidized with Al and the requisite amount of borate added according to the slag bulk. The final additions of Al (about 2 lb./ton) and low-carbon ferro-titanium (4 lb./ton), or alternatively excess Al, should be made either to the bath or during tapping.

Open-Hearth Furnaces—The additions would be made to the ladle, the Al, ferro-titanium, and borate being mixed and added at the beginning of tapping. It would be necessary, however, to prevent the follow-through of the tapping slag.

Acknowledgments

The author thanks the Directors of The United Steel Companies, Ltd., and Mr. F. H. Saniter, Director of Research, for permission to publish this paper. The interest shown by Mr. F. H. Saniter, Mr. W. E. Bardgett, and other colleagues is greatly appreciated. Grateful acknowledgment is made to Mr. G. Padget and other members of the Chemical Section for their valuable contribution.

References

1. G. Derge : *Trans. Amer. Inst. Min. Met. Eng.*, 1946, *Metals Technology, T.P.* 2004.
2. W. E. Bardgett and L. Reeve : *J. Iron Steel Inst.*, 1949, vol. 163, pp. 277–294.
3. G. A. Rudolph and L. C. Flickinger : *Steel*, 1943, vol. 112, Apr. 5, pp. 114, 131, 149.
4. The United Steel Companies, Ltd. : " Standard Methods of Analysis of Iron, Steel, and Ferro-Alloys," pp. 10–12. Fourth edition, 1951.
5. G. E. Speight : *J. Iron Steel Inst.*, 1950, vol. 166, pp. 196–198.
6. R. W. Gurry : *Trans. Amer. Inst. Min. Met. Eng.*, 1943, *Metals Technology, T.P.* 1641.

Sub-Surface Ingot Structure of Semi-Killed Steel

By R. Wogin, B.Sc., A.Met., A.I.M., and A. Goodall

SYNOPSIS

The sub-surface ingot structure of semi-killed plate steel, made in 10-ton slab-type moulds, is discussed after examination of more than 250 casts. The structural variation at various carbon levels is traced and demonstrated pictorially from the stage at which the steel might be termed 'rimming' to that at which it might be termed 'killed.' The semi-killed series are classified into (1) rimming, (2) intermediate, and (3) ladle-balanced types. The characteristics of each are discussed.

The mould addition is claimed to give a good indication of the structure at a particular carbon level and, from this, mould control is developed. It is possible to apply this knowledge to minimize defects by preferential ingot treatment in the mill.

It is shown that a treatment developed for short slaggy ladles—which are consequent to tilting-furnace practice—can reduce defects.

Although the intermediate type of semi-killed steel has given the most defects, this type of ingot can produce a clean plate under certain conditions. It is concluded that rolling-mill practice has an appreciable effect on plate defects.

Most of the steel made within the authors' plant is semi-killed and is cast into 4-ton and 10-ton ingots.

In the 4-ton ingots used for structural sections, teemed relatively quickly and set with 1–2 lb. of Al in the top 6 in. of the mould, the incidence of surface defects (mainly crack and shell) is related to teeming temperature (ladle skull), nozzle size, and sulphur content.[1]

In the slower-teemed 10-ton ingots used for plates, the causes of such defects are not so obvious. Plate defects of the spongy and seamy type are generally agreed to be related to sub-surface blowholes. There appears to be a critical skin thickness for a particular heating practice. With a skin thicker than the critical, scaling in the soakers and reheaters will not give spongy or seamy defects unless the heating is greatly prolonged. On the other hand, a very thin-skinned ingot may well have both skin and blowhole zone removed during normal heating and so give a clean plate surface. The defects probably arise in ingots somewhere between these limits.

Reference has been confined mainly to the lower-carbon series since more information was available at the time.

OBJECT OF THE INVESTIGATION

The object of the investigation was to find the average sub-surface ingot structure produced by any given amount of ladle deoxidizer (silico-manganese) over the whole range of semi-killed steels. The range examined is much wider than that made in normal production.

Further experiments were made to find the quantitative effect of other variables on the sub-surface ingot structures, and a study was made of the defectives associated with the different types of semi-killed ingot at one particular carbon level.

GENERAL PROCEDURE

The investigation was conducted on 10-ton slab-type ingots intended for boiler and ship plate. The furnaces used were 300-ton tilting, working a phosphoric iron, and were unique in that two or three 80-ton ladles could be tapped from the same bath for comparative purposes. The steel was brought to specification in the ladle by adding anthracite, ferro-manganese, and silico-manganese (20% Si). The temperature differential through the bath was 9° C./ft., with a bath depth of 3 ft. 6 in. The furnaces were operated normally and were tapped with a slag iron of 11·0–13·5%.

Successive ladles were paired to show the ingot structures associated with :

(*a*) Varying silico-manganese additions for the same carbon content

(*b*) Constant silico-manganese addition for varying carbon contents.

Unless otherwise stated, all ingots were set in the top by adding Alsimin (35% Si–50% Al) during the last 6 in. of teeming. The term 'mould addition' indicates the amount of Alsimin required to give a flat or slightly convex top to the ingot.

From each of more than 250 casts examined the middle of the ingot was taken as representative and was corner-sampled at top, middle, and bottom positions.[2] For investigation of blowhole length on rimming types, it may be advisable to adopt the drilling method used by Jackson.[3]

In assessing the results the middle corner sample has normally been found to be representative of the ingot. However, on the thick-skinned ingots (type *D*) the gas reaction may be so vigorous that, at the time of the mould addition, blowhole formation may not be complete at the middle of the ingot. The bottom sample has therefore been used.

EFFECT OF SILICO-MANGANESE LADLE ADDITIONS

The average structure for each pit carbon and ladle silico-manganese level is shown in Fig. 5. The zones *D*, *C*, *B*, and *A* cover, in that order, the transition from the rimming type towards the killed steels. The main features are as follows :

(*a*)—*With increasing silico-manganese in the ladle:*

(1) The skin becomes thinner until the blowholes are substantially surfaced (less than $\frac{1}{8}$-in. skin)

(2) Until this surfacing occurs, the *length* of the blowholes is relatively unchanged ; further silico-manganese addition then progressively shortens the holes until they disappear

(3) The mould addition decreases

(*b*)—*With constant silico-manganese addition to the ladle, and increasing carbon content:*

(1) The skin thickness of rimming-type ingots decreases

(2) The lenticular type of blowhole becomes shorter and more ovoid

(3) The mould addition decreases.

Manuscript received 12th March, 1951.

Mr. Wogin is Manager of the Appleby Melting Shop, and Mr. Goodall is Senior Assistant in the Steelworks Section of the Metallurgical Department at the Appleby-Frodingham Steel Company, Scunthorpe, Lincs.

CLASSIFICATION AND CHARACTERISTICS OF SEMI-KILLED STEEL

On the findings of Fig. 5, it is considered that there are three types of semi-killed steel: (1) Rimming (type *D*), (2) ladle-balanced (type *A*), and (3) intermediate (types *B* and *C*).

Rimming Type (*D*)

The skin thickness of type *D* is more than $\frac{3}{16}$ in. It is truly rimming in its characteristics, for the blowholes tend to be localized in the lower portion of the ingot. Blowhole development is arrested on making the mould addition. In general, the thicker the skin the shorter is the distance up the ingot over which the blowholes occur.

A small decrease in the state of oxidation seems to extend the blowholes higher, and in a proportion of casts they were found at least to the point at which the mould addition was made. The structure of the top portion of the ingot is most variable and the majority of seamy or spongy plate defect comes from the bottom two-thirds.

Should insufficient mould addition be made so that the top is allowed to 'work,' the blowhole length will be increased and the zone will extend to the top of the ingot. The effect is illustrated in Fig. 6 for type *D* and type *C* ingots.

A $\frac{3}{16}$-in. skin will protect an ingot through normal soaker practice, but if certain ingots have to be soaked for excessive periods, then, to prevent the defects caused by the surfacing of blowholes, a thicker skin will be required.

Knowledge of the open-hearth process and of the factors of deoxidation is insufficient at present to control the skin thickness of this type of steel to within $\frac{1}{8}$ in. so that, for the average ingot, a skin somewhat thicker than $\frac{3}{16}$ in. must be the objective. It is worthy of note that a skin more than $\frac{1}{2}$ in. thick can be produced at 0·27% carbon.

Ladle-Balanced Type (*A*)

Type *A* represents an ingot with surface blowholes less than $\frac{1}{4}$ in. long and about $\frac{1}{64}$-in. dia. Correctly balanced in the ladle, an ingot can be produced which is completely solid to at least 2 in. below the surface, without any mould addition whatever, but not without the possibility of pipe losses.

Intermediate Type (*B* and *C*)

Between the rimming and the ladle-balanced semi-killed steels there is a fairly wide range where the blowholes are less than $\frac{1}{8}$ in. from the surface and may exceed 1 in. in length. They may touch the surface. The blowholes will be exposed in soaking, broken open in rolling the ingot, or will remain only lightly covered in the slab. This may be persistent and cause losses in the plate as seamy or spongy defect.

DEFECTIVES PRODUCED FROM EACH TYPE

The frequency of defectives for a 0·10% carbon steel is shown in Figs. 1*a*, 2*a*, and 3*a*, which represent 26,000 slabs, or approximately 40,000 tons. Figure 1*a* gives an index for losses in the slab mill. This mill supplies two separate plate mills, the defectives from which are indexed in Figs. 2*a* and 3*a*. Only slabs charged hot to the reheaters are considered.

A different index has been used for slab defects, and comparison cannot be made between slabs and plates. Also, 'slab defect' does not represent scrap material. These so-called defective slabs are cooled and torch-dressed, as opposed to the normal practice of charging slabs hot into the reheaters.

Type *D* was produced by adding no silicon to the ladle and as such would have a rather thick skin.

The main feature is the high seamy and spongy losses from type *C* ingots and the high blister, pipe, and lamination losses from the thick-skin type *D*. Any lamination in the top third of the ingot is designated as pipe, which is then by far the highest of these three defects.

The somewhat lower crack and shell frequency in the slab stage for type *C* ingots is countered by the higher spongy and seamy frequency. Spongy defect, however, is more difficult to 'dress' and may tend towards higher scrap losses.

PIPE LOSSES

It must be assumed that after the top is solid, and as the ingot cools, some gas evolution takes place within the ingot. Although the corner samples are usually solid below the blowhole zone, there must be other gas cavities within the ingot which reduce the pipe.

Rimming Type (*D*)

By far the heaviest pipe losses, for 0·10% carbon steel in plate manufacture, arise from type *D* where no silicon has been added to the ladle. This is not a true rimming steel, of the type made for sheet and strip, since the total iron in the slag rarely exceeds 13·5%; nevertheless the skin thickness may exceed $\frac{1}{2}$ in. Although lenticular blowhole formation appears to cease as the top is 'set,' gas may arise through the still-liquid centre to form an upper cavity rather than a general scatter of secondary blowholes. Alternatively the so-called pipe may be central porosity related to the rather large mould addition and the 10-ton ingot size. It would seem preferable to make this addition after teeming is complete to avoid inclusions being carried down the ingot, but such a method with so large an addition can easily result in a badly worked top (*see* Fig. 6). This ingot would then show still heavier pipe losses, presumably due to extrusion of the steel from the top. The whole blowhole zone is extended when the top has worked and may exceed $1\frac{3}{4}$ in., but the skin thickness is unaffected.

Ladle-Balanced Type (*A*)

Pipe losses are slightly higher with type *A* than with types *B* and *C*, but are not unduly high unless the silicon is much above 0·05%. The fine control of producing a surface free from blowholes and yet sufficient gas to minimize the pipe is of course the derivation of the term 'balanced.' A 'solid' ingot *can* be produced without the residual silicon exceeding 0·06% but it is advisable to make a ladle addition that is just short of this and to prevent the formation of fine acicular blowholes by a small 'all the way' mould addition, rather than to risk pipe losses from the bath which is more 'dead' than usual.

The term 'solid' is applied where no blowholes are

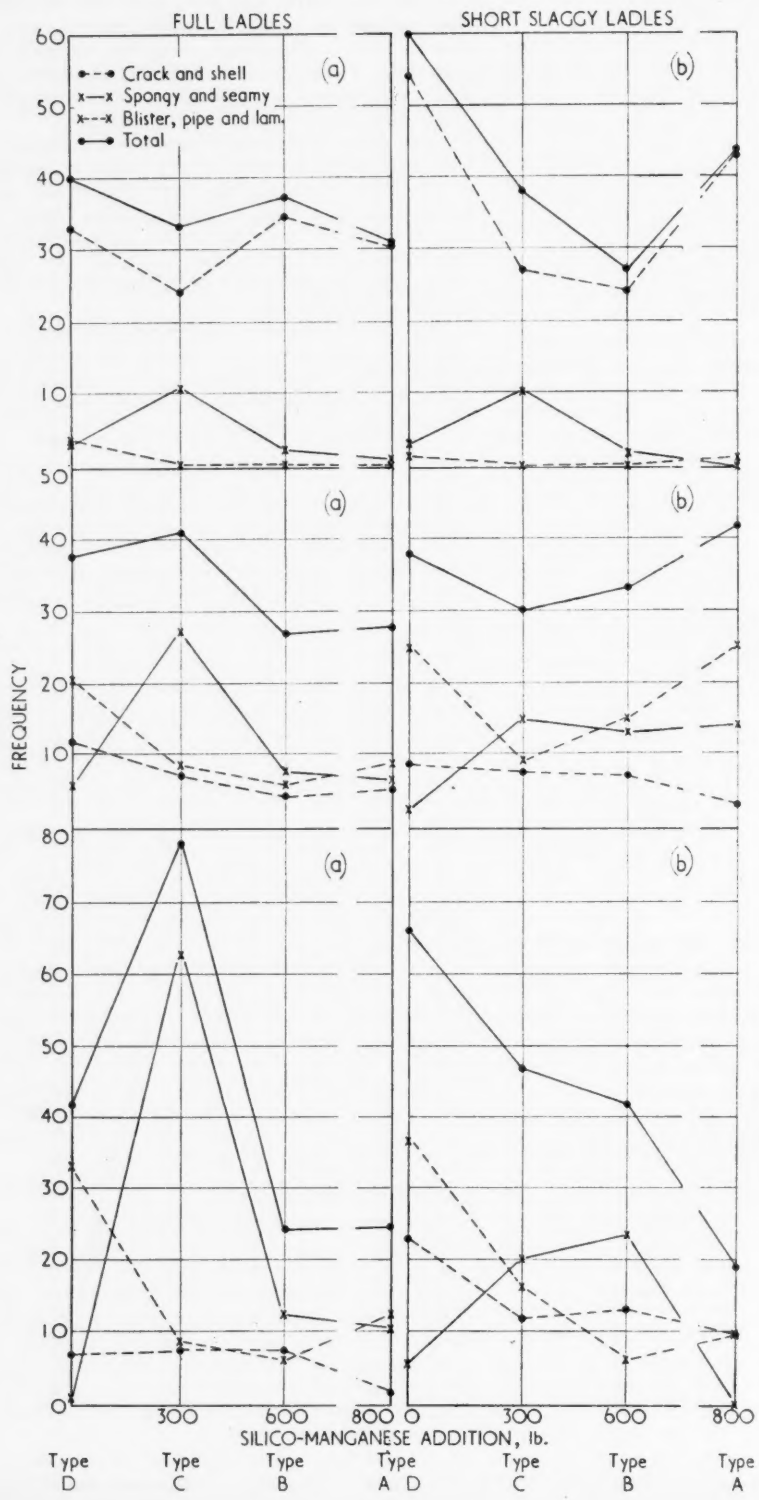


Fig. 1—Frequency of slab defects

Fig. 2—Frequency of plate defects (for hot-charged slabs); No. 1 mill

Fig. 3—Frequency of plate defects (for hot-charged slabs); No. 2 mill. Note—There are relatively few ingots in the 800-lb. group for No. 2 mill

apparent within the ingot corner samples, that is, to a depth of approximately 3 in. In the top section, particularly with types *B* and *C*, a more gross type of blowhole may appear beneath the surface zone. This is referred to as a blown top.

A type *A* ingot can have a top corner section which is not blown, even with no mould addition, and yet show a slight dome. The distribution of the deep-set holes, which are calculated to balance the pipe in such an ingot, is an interesting speculation.

SEAMY AND SPONGY LOSSES

The chances of producing spongy or seamy defects are undoubtedly high with type *C* ingots. With type *B* there is a better chance of the blowholes being washed off during reheating of the slab after the holes have decreased in length by ingot-to-slab reduction.

It is a matter of conjecture whether the fine lenticular type of blowhole or the rounded ovoid is the least desirable where surfacing occurs. There is some evidence that a lenticular hole will persistently hold scale and in consequence produce a defect, where a larger ovoid may remain plastic and be deformed to conform with the surface.

ASSOCIATED EXPERIMENTS

Ingot Structure through a Heat

To justify the use of the middle ingot of a cast for sampling purposes the sub-surface structures of several complete casts were examined.

Figure 9 shows the high degree of similarity between ingots on a cast of type *A* or *B*. The top of No. 3 ingot was cleared by an early mould addition as a separate experiment.

Figure 10 shows a heat of type *D* ingots slowly teemed through a 1-in. nozzle. Excluding No. 5 ingot, which was check-teemed, the skin thickness follows the teeming curve (*see* below) and the middle ingot has a skin thinner than the average. To take the middle ingot of such a cast is in the interest of the practical interpretation, which in this case is concerned with the protection of the blowholes from exposure.

Teeming Speed

The teeming speed for each ingot of a cast using the normal 1-in. or 1½-in. nozzle is shown in Fig. 4. The effects of varying the teeming can be exaggerated by check-teeming through a partly closed nozzle. Figure 10, where the teeming speed of No. 5 ingot has been almost halved by check-teeming, shows that the skin thickness on type *D* ingots is roughly inversely proportional to the rate of rise up the mould.

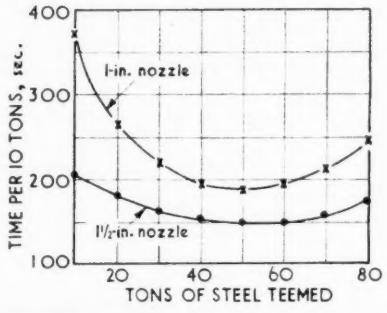


Fig. 4—Teeming speeds using 1-in. and 1½-in. nozzles

The fact that a thicker skin can be produced later in the heat, despite a faster rate of teeming (343 sec. for No. 5 ingot against 367 sec. for No. 1) raises an interesting point. It could well be assumed that the later ingots of a heat would be teemed at a lower temperature and therefore that a lower temperature will thicken the skin. Land[4] contends that the temperature of teeming does not fall through a heat and the authors' immersion tests confirm this. However, check-teeming may cool the steel owing to some spreading of the stream and a lower temperature may be associated with a thicker skin.

Evidence has so far indicated that factors which thicken the skin of a type *D* ingot tend to alter a type *A* to a type *B* ingot. Thus slow-teeming a type *A* or *B* ingot might be expected either to lengthen the blowholes or to thicken the skin. Figure 11 shows that neither is the case; decreasing the teeming speed 2½ times has produced no appreciable difference in the sub-surface structure.

The findings on the type *D* ingot agree with the conception of a rimming steel. Any factor which accelerates or prolongs the gas reaction 'to sweep the rim' results in increased thickness of skin. With types *A* or *B* the FeO concentration is so low that variations in teeming speed do not affect the reaction. Blowhole formation on these types is apparently unaffected by the rate at which a ferrostatic head is produced.

These results have considerable practical value. The skin thickness of a type *D* heat can be altered by the nozzle diameter. With type *A* or *B* ingots the steel can be teemed rapidly through a 2-in. nozzle without affecting the sub-surface structure.

Effect of a Brick Head

With the rimming type *D* an aluminium addition must be made to the mould when full to suppress gas evolution for a length of time sufficient to allow the top to set, before evolution again begins. With a correctly ladle-balanced type *A* ingot no such addition is necessary as insufficient gas is involved to keep the top open and the ingot will set itself. An ingot takes some 60 sec. to crust over and it would seem reasonable to expect that the time the top is 'open' would influence the blowhole length. Experiments on type *D*, using a brick head, indicate that, although the skin thickness remains the same, the blowholes increase in size. A brick head seems to have little effect on the blowholes of type *B* (Fig. 7).

Significance of the Mould Addition

In Fig. 5 Alsimin was added in the last few inches of teeming (the quantity required is shown in each case). The mould addition gives a reasonable indication of the ingot structure for a particular carbon specification level. It can be utilized in practice to indicate the skin thickness of the thicker-skinned ingots of type *D* or in the identification of types *A*, *B*, or *C*. Thus, for a type *A* ingot, using 600 lb. of silico-manganese on a 0·11% carbon specification, no more than 1 lb. of Alsimin would normally be required. If, for some reason, the actual mould

requirement was 3–4 lb., then the ingot would be type *B* or even type *C*.

Such knowledge shows the possibilities of a mill control designed to utilize the characteristics of the ingot structure. For example, the mould addition may suggest that the ingot is type *C*. Type *C* ingots show much less spongy and seamy defects if the slabs are allowed to go cold before reheating, and a type *C* ingot would best be used as stock slabs. Similarly, a thicker skin is required to resist the heavy soaking of the weekend charge or of a breakdown period, for which type *D* ingots would be the most suitable.

For comparison, aluminium may be considered 1½ times as effective as Alsimin.

Method of Making the Mould Addition

On No. 3 ingot of Fig. 9, showing a type *B* heat, the mould addition has been made 18 in. down, that is, just below the top corner sample. The top of the ingot is cleared of surface blowholes. On the other ingots, added in the last 6 in. of teeming, the Alsimin has merely prevented the top from working and the blowhole zone from growing.

The mould addition is effective only above the point at which it is added. Although the stream carries the products of deoxidation down the ingot, Alsimin cannot eliminate blowholes which have already formed.

Figure 12 shows, on a type *C* ingot, the effect of making the addition all the way up the mould. The blowholes have been considerably shortened. With a type *A* or *B* ingot where the blowholes are already very small, a progressive addition may clear the holes completely.

With a type *D* ingot the mould addition presumably suppresses gas evolution for a sufficient time to allow the ingot top to crust over. Assuming the top does not work, the sub-surface structure is that developed at the time of making the mould addition. On this type of ingot the Alsimin should be added as late as possible to avoid the products of deoxidation being carried down the ingot by the stream. It would be preferable, were it practicable, to puddle-in the Alsimin after teeming has ceased.

Effect of Slag on the Ladle and Ingot Structure from 'Short' Ladles

In large tilting-furnace practice, although 40 tons of phosphoric slag are removed from the furnace 2 or 3 hr. before tapping, the refining slag on the last ladle tapped contains 14% of P_2O_5 and can cause phosphorus reversion. In general, with a ladle weight above 25 tons this slag causes the ingot structure to change from type *A* towards type *D*. It is only on very short ladles that the silicon concentration may reverse the trend, and these are exceptional cases.

The type of distribution obtained is shown in the following figures from 46 random casts of 0·08–0·10% carbon steel with a 600-lb. silico-manganese ladle addition; type *B* is the average ingot for the casts without slag:

	Without Slag			With Slag		
Type	Mould Addition, lb.	Casts %	Casts No.	Mould Addition, lb.	Casts %	Casts No.
A and *B*	0–4	68	17	0–2	33	7
C	½	32	8	½–4	43	9
D	...	...	...	5–12	24	5

Six of the eight casts under type *C*, without slag, had late bath additions (within 40 min. of tap); this had no effect upon the ingot structure. In these tests 10 min. was allowed between the addition and filling the ladles.

This general movement of ingot structure towards the type *D* ingot, for any given silico-manganese addition, was confirmed by an analysis of the defectives for short slaggy ladles made over the same period as the casts shown in Figs. 1*a*, 2*a*, and 3*a*. A ladle was considered slaggy if it was 10 tons or more below its nominal capacity or if the phosphorus in the pit sample was more than 0·008% higher than on the previous ladle. The defective frequency is shown in Figs. 1*b*, 2*b*, and 3*b*.

On full ladles the type *C* ingot gives the highest spongy and seamy losses and is produced with 300 lb. of silico-manganese. With short slaggy ladles type *C* will normally be produced with appreciably more than 300 lb.—the highest seamy and spongy losses are at 300–800 lb. In practice, this means that if the ladle-balanced type (*A* or *B*) is normally made, then the slaggy ladles will have the higher proportion of type *C* ingots and will give the most spongy or seamy defect. If type *C* ingots were the normal aim, the slaggy ladles would have a protective type *D* skin and would show the least spongy and seamy. With type *D* ingots, slag will merely thicken the skin, and the graphs indicate that this may lead to higher pipe, lamination, and blister loss. Slag improves a type *C*, but worsens a type *A* or *B* aim.

It may be considered advisable to make low-carbon steel ladle-balanced to avoid the top segregation and piping of the suppressed rimming type. A control system for short slaggy ladles was tried when, to avoid this piping, the normal addition to a 0·10% carbon steel would be 600–800 lb. of silico-manganese. With a ladle weight above 50 tons, 800 lb. of silico-manganese ensured type *A* or *B*. A progressive mould addition corrected any variations. With a ladle weight below 50 tons it was considered impossible to ensure a ladle-balanced steel and 200 lb. of silico-manganese were added to produce a type *D* ingot. On the odd occasion, due to a very small ladle weight, the 200-lb. addition produced an ingot with little or no skin. This was apparent from the small mould addition required—usually below 4 lb.—and in this case Alsimin was added as a progressive addition to clear the surface holes (*see* Fig. 8).

FACTORS WHICH CHANGE THE STRUCTURE FROM TYPE *A* TOWARDS TYPE *D*

The following is a summary of the factors which change an ingot structure from type *A* towards type *D* (*see* also Fig. 10):

(1) Less ladle deoxidant. The effect per unit decrement increases as the ladle addition decreases.

(2) Lower carbon specification. It should be recognized, however, that a skin thickness of ½ in. or more can be produced at 0·27% of carbon.

(3) Slow teeming. This has a pronounced effect on thickening the skin of type *D* ingots, but it has little effect on types *A* or *B*. It would seem that skin formation—that is, a slight rimming action—must occur before teeming speed has any effect.

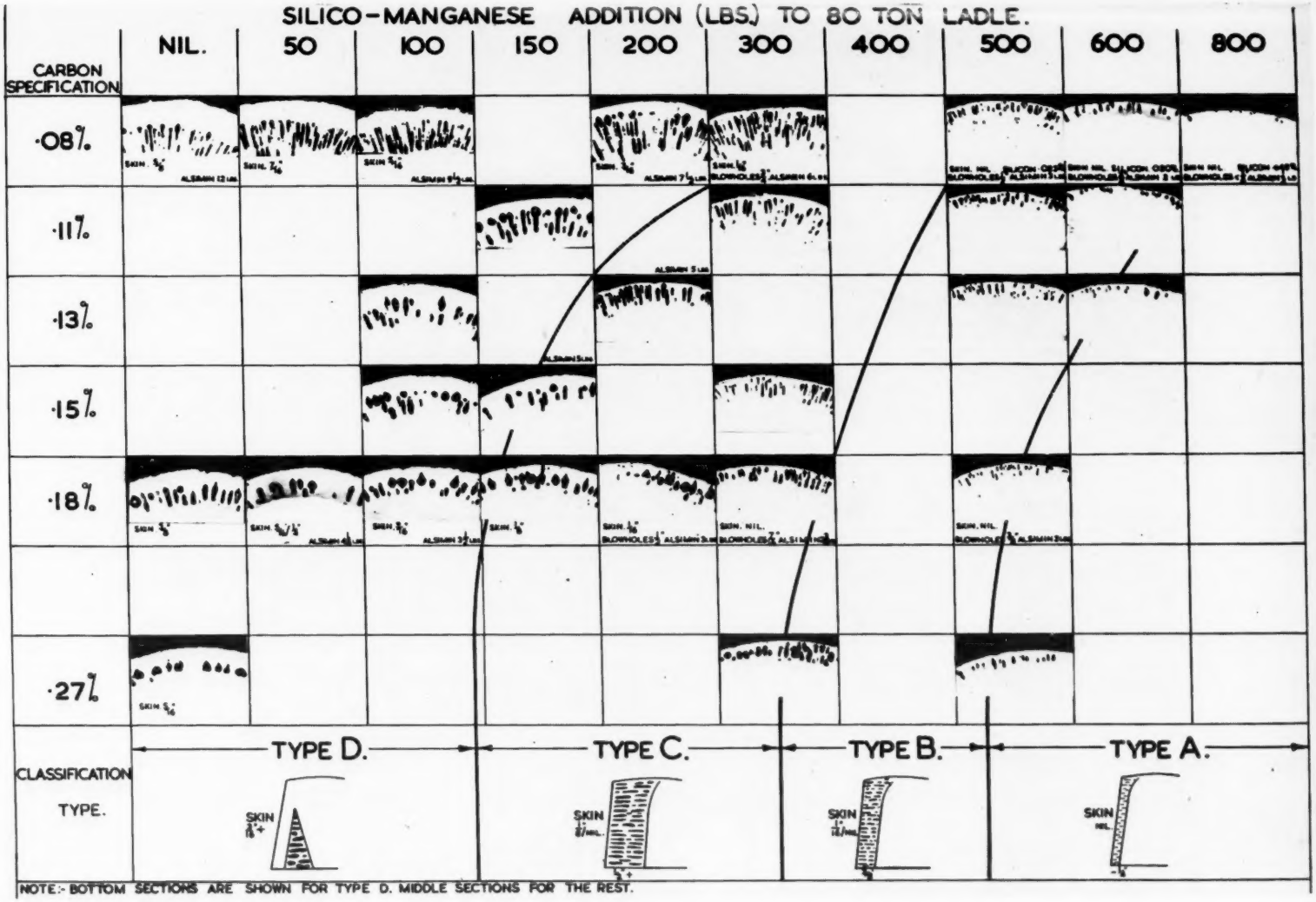
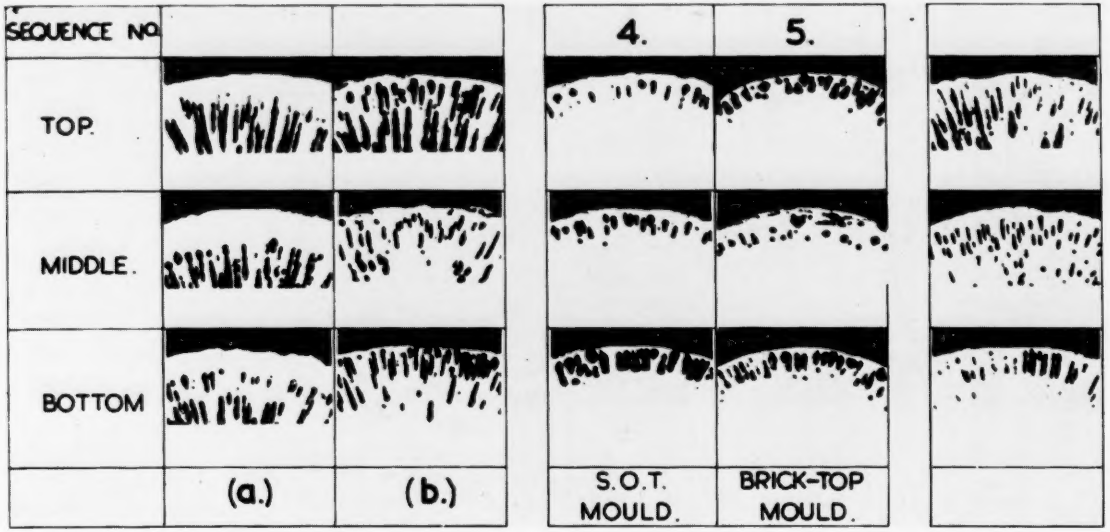


Fig. 5—Classification of the ingot structure of semi-killed steel (10-ton slab-type moulds) (Three-eighths actual size)

[Wiggin and Goodall
[To face p. 158



(*a*) 200 lb. of Si-Mn, 5 lb. of Alsimin (but requiring 9 lb.) in mould; type *D*
(*b*) 600 lb. of Si-Mn, 2 lb. of Alsimin (but requiring 4 lb.); type *C*

Fig. 6—Badly 'worked' tops: 0·10% C

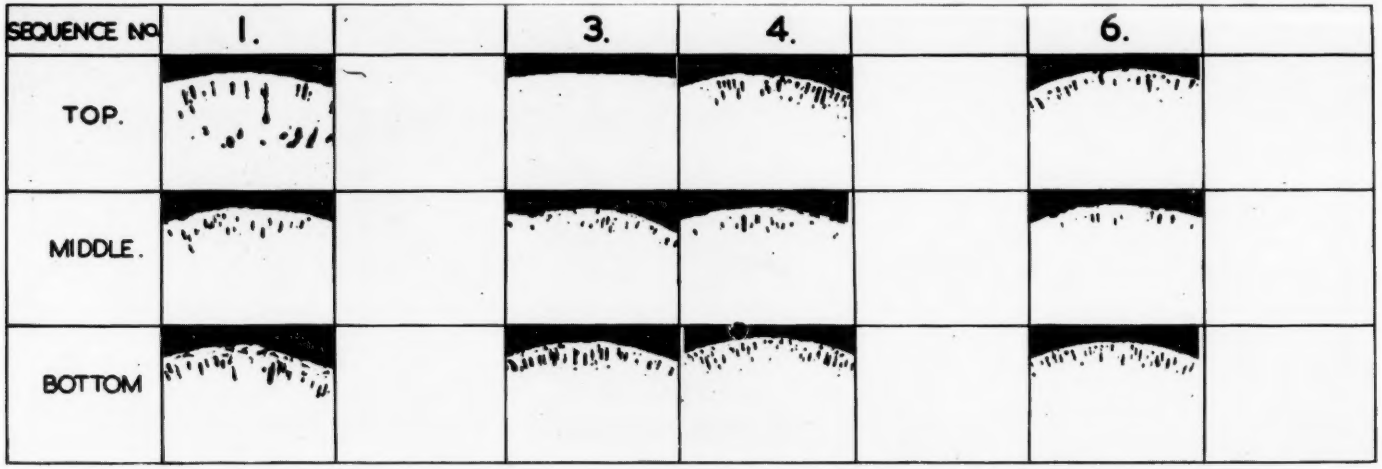
No. 4 ingot: 2 lb. of Alsimin in last 6 in.
No. 5 ingot: No mould addition, Lapex cover

Fig. 7—Two successive ingots from a type *B* heat, showing that a brick head has little effect on the sub-surface structure

0·09% C; 200 lb. of Si-Mn; 2 lb. of Alsimin in last 6 in. (domed top)—such ladles normally require more than 7 lb. of Alsimin

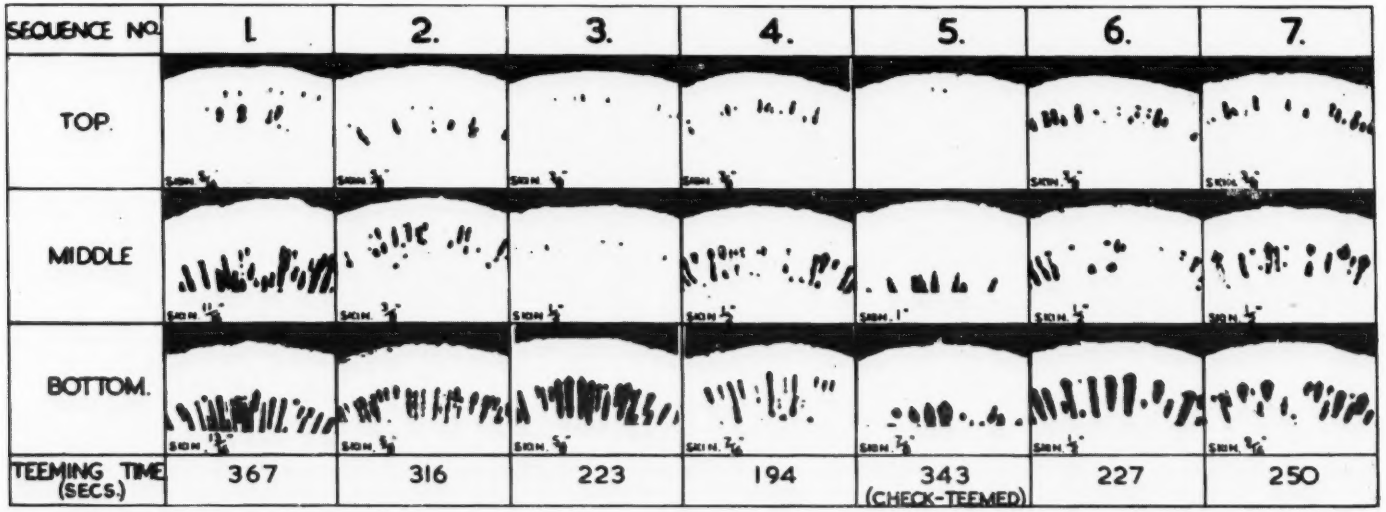
Fig. 8—Ingot cast from a short slaggy ladle requiring exceptionally low mould addition, showing that the mould addition gives a good indication of the ingot structure

(Figs. 6, 7, and 8 two-fifths actual size)



1¼-in. nozzle, ingots numbered in sequence of teeming. 0·15% C; 500 lb. of Si-Mn; 2 lb. of Alsimin; ladle skull 'plate.' On No. 3 ingot mould addition was made just below point at which top corner sample was taken, otherwise addition was in last 6 in. of teeming. Al-imin reduces blowholes only above the point at which it is added.

Fig. 9—Four ingots from a type *B* heat, showing similarity of structure within the heat

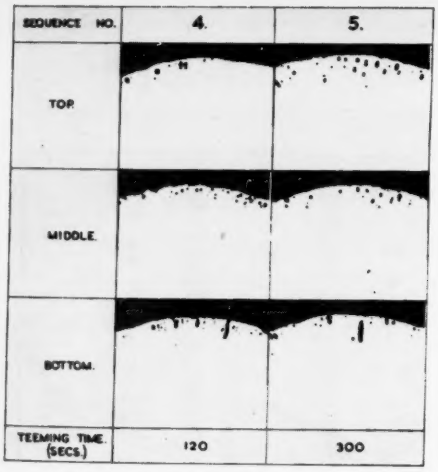


1-in. nozzle, ingots numbered in sequence of teeming; No. 5 ingot check-teemed. 0·15% C; 50 lb. of Si-Mn; 7 lb. of Alsimin; ladle skull 'part-plate'

Fig. 10—Heat of type *D* ingots, showing that teeming speed has a pronounced effect on the skin thickness of type *D* ingots

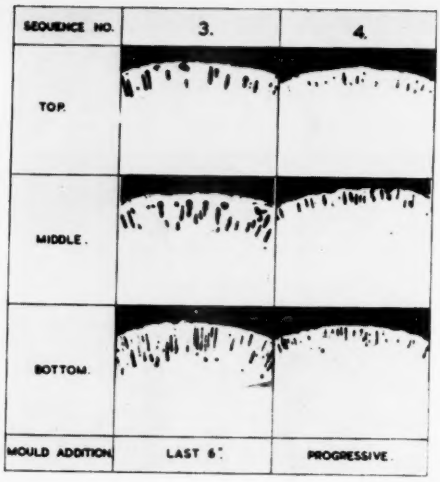
(Figs. 9 and 10 two-fifths actual size)

[Tegelin and Goodall



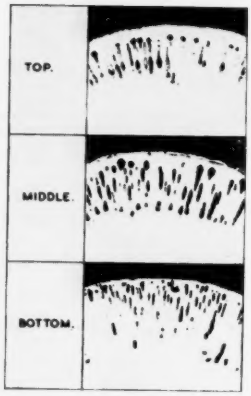
2-in. nozzle; No. 5 ingot check-teemed. 0·15% C; 600 lb. of Si-Mn; 1 lb. of Alsimin; ladle skull—'plate'

Fig. 11—Two successive ingots from a type *A* heat, showing that teeming speed has little effect on type *A* ingots



1-in. nozzle; 0·08% C; 600 lb. of Si-Mn; 2½ lb. of Alsimin; ladle skull—'plate'

Fig. 12—Two successive ingots from a type *C* heat, showing that Alsimin added progressively reduces the length of the blowholes



1¼-in. nozzle; 0·11% C; 200 lb. of Si-Mn; 5 lb. of Alsimin; ladle skull—'plate'

Fig. 13—Type *C* ingot which did not produce any defective plates

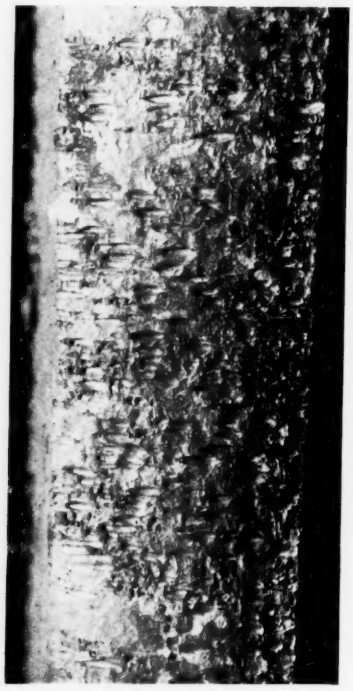


Fig. 14—Surface of the middle slab rolled from the ingot shown in Fig. 13. Blowholes had been 'surfaced' at this stage

(Figs. 11, 12, and 13 two-fifths actual size; Fig. 14 actual size)

(4) High mould requirements as a late addition. The different level of this addition according to the carbon specification is most marked. With due allowance for this, the mould addition is an indication of the sub-surface structure.

(5) Slag on the ladle. The effect is pronounced but the degree is so variable that no pair of casts (with and without slag) could be chosen as typical. No quantitative result is possible, particularly with a variable ladle weight.

These factors in reverse change the structure from type *D* towards type *A*. A factor of practical importance which also has this effect is the progressive mould addition.

DISCUSSION

For any given quality made with a standard ladle deoxidation practice, there will be some variation in sub-surface ingot structure. This variation, probably about $\frac{1}{8}$-in. skin thickness with small ladle silicomanganese additions, is thought to be due to (*a*) variations in the state of oxidation of the bath, (*b*) differences in the temperature at which the steel is teemed, and (*c*) variation in teeming rate.

Accepting such a degree of variation, it is unlikely that all ingots of the thick-skinned type will be able to meet the different ingot heating conditions without some having the blowholes exposed. These surfaces will be oxidized either in the soakers or in the reheaters. In the event of a bad cast it is necessary to formulate the reason for this from a knowledge of the type of sub-surface structure involved and the mill history of the cast. It is important to know why a particular sub-surface structure does not always give defects, for this knowledge will define the contribution which mill control can make to the reduction of defectives.

In an experiment originally carried out to find the effect of plate and slab thickness on surface condition, a thin-skinned (type *C*) ingot with rather long blowholes was charged cold and cogged down to slabs 8 in. and 5 in. thick. It had the type of sub-surface structure from which seamy and spongy defects would be expected.

The ingot structure is shown in Fig. 13, and Fig. 14 shows the surface of the slabs rolled from this ingot ; this particular section was a middle slab. The blowholes occur as shallow ovoids in or on the slab surface.

Adjacent slabs from this ingot were charged hot and cold into the reheaters. The plate thickness ranged from $\frac{1}{4}$ to $\frac{3}{4}$ in. The plates gave no defect whatever, the surfaces being perfectly clean. It is considered that the already surfaced remains of the blowhole structure were entirely removed in the reheaters, even on the hot-charged slabs with their relatively short heating time.

It has been shown previously that this type *C* ingot does result in higher defective losses, particularly sponginess and seaminess. This experiment shows that mill practice has a considerable influence on defectives and that it is by no means certain that a bad ingot structure will lead to a defective plate.

CONCLUSIONS

(1) Within the practical limits of these experiments the middle ingot is reasonably characteristic of a heat.

(2) Marked changes in sub-surface ingot structure can be achieved by varying the amount of deoxidizer added to the ladle. The quantitative effect per unit variation is greater at the lower levels of silicomanganese and differs for each carbon specification. Carbon added to the ladle also acts as a mild deoxidizer.

(3) There are three kinds of semi-killed steel : rimming, intermediate, and ladle-balanced ; each has its own characteristics.

(4) As a top addition, the mould requirement is an indication of the sub-surface structure at a particular carbon level. This mould addition will only remove blowholes above the point at which it is added or will halt their formation by suppressing a rimming action.

(5) A progressive addition to the mould, in amount similar to that required in the top, will result in an appreciable movement in the type of sub-surface structure towards the ladle-balanced type. This fact offers a practical means of correction in the mould ; *viz.*, a means of altering an intermediate type to a ladle-balanced type.

(6) Teeming speed has a pronounced effect on the rimming type of semi-killed steel and slower teeming may well be used to thicken the skin.

With the ladle-balanced type the teeming rate has little effect and the nozzle size may be selected to suit other conditions.

(7) A brick head appears to have no effect on the skin thickness of rimming-type ingots and no appreciable effect on the blowhole length of the ladle-balanced type.

(8) Slag on a ladle will usually result in a sub-surface structure nearer the rimming type than would otherwise have been the case. Control of very short ladles may be attained by making only the rimming type of semi-killed steel.

(9) For low-carbon steels spongy and seamy defects come mainly from the intermediate type of sub-surface structure. They can be minimized by making either the rimming or the ladle-balanced type. A thick-skinned rimming type is liable to show pipe losses.

(10) Where slabs are reheated mill practice has a considerable influence on defectives.

(11) The higher-carbon series follow the same pattern and any differences may be due to their being used for thicker slabs and plates.

Acknowledgments

The authors thank the Management of the Appleby-Frodingham Steel Company for permission to publish this paper.

They are indebted to Mr. A. Jackson, who sponsored and encouraged the work, and they acknowledge assistance from the staff of the Appleby melting shop and mills, the metallurgical department, and the members of the Steel Quality Group.

References

1. L. REEVE : *J. Iron Steel Inst.*, 1948, vol. 160, pp. 169–176.
2. *J. Iron Steel Inst.*, 1950, vol. 165, p. 54.
3. A. JACKSON : " Rimming Steels," *Swansea Met. Soc.*, 1936, Jan. ; " Notes on Rimming and Semi-Killed Steels," *Newport Met. Soc.*, 1936, Nov.
4. T. LAND : *J. Iron Steel Inst.*, 1941, No. II, p. 157P.

XUM

Magnetostriction of Some Ferromagnetic Alloys

By E. W. Lee, B.Sc.

SYNOPSIS

A simple apparatus is described which comprises a double roller and mirror system and is capable of giving accurate measurements of magnetostriction of ferromagnetic rods. The apparatus was used to study the magnetostriction of some alloys, including the Ni–Co system; from the latter, some conclusions concerning the variation of λ_{100} with composition have been drawn. The temperature coefficients of magnetostriction of four nickel alloys have been measured.

It has been shown, chiefly by Becker *et al.*,[1] that many intrinsic properties of ferromagnetics, *e.g.*, behaviour under tension and, in some materials, coercivity and initial susceptibility, are determined very largely by their magnetostriction properties. Many investigations into the magnetostrictive behaviour of ferromagnetics have been carried out, but the amount of useful information generally available is very small. In several cases measurements have been made on alloys with low Curie temperatures, and many workers have failed to distinguish between magnetostriction caused by domain vector rotations and that caused by changes in spontaneous magnetization. Moreover, unless the materials investigated have perfectly random distributions of domain vectors in the demagnetized state, the measurements are bound to be in error if the magnetic field is not applied in two directions, parallel and perpendicular to the same direction of strain measurement. This has not yet been attempted.

Bates and his co-workers[2, 3] recognized, during the early investigations of the thermal changes accompanying magnetization, that the general character of the curves obtained was closely related to the magnetostrictive behaviour of the various materials. The results of an investigation[2] into the thermal changes found in materials under tension showed that the thermal curves fall into two distinct groups, the magnetostriction being either positive or negative.

More recently, Stoner and Rhodes[4] put forward a theoretical interpretation of these curves and developed expressions which would enable the heat changes to be calculated if sufficient data were known. The information required includes the saturation magnetostriction and its temperature coefficient. The only material for which both these quantities are known is nickel, and although some data are available for most of the simple alloys, nothing is known of the magnetostriction of some of the alloys investigated by Bates and Harrison.[3] It seemed likely, therefore, that if this information could be obtained it would help to explain the thermal changes found by these workers.

APPARATUS AND EXPERIMENTAL DETAILS

The specimens used were rods 40 cm. long × 4 mm. dia. This shape excludes any possibility of making measurements with the field applied in two perpendicular directions, but the usual errors inherent in assuming a completely random demagnetized state may be present.

The accurate measurement of magnetostriction is difficult, the problem being not so much that of providing a large magnification of a small movement but of ensuring that the results obtained are accurately reproducible. Accurate measurements can only be obtained if the specimen is of suitable shape. The apparatus comprising a roller and an optical lever (Nagaoka[5]) was used because of its extreme simplicity and because of the shape of the present specimens.

The two main sources of error are (*a*) translational and rotational forces on the specimen in the magnetic field, and (*b*) bending of the specimen if it is already slightly bent (this nearly always occurs with rods of these dimensions). Errors due to (*a*) can be avoided only by accurate placing of the specimen in the solenoid, and errors due to (*b*) are eliminated by using a double roller system.

The principle of the extensometer system may be seen from Fig. 1. A hollow rectangular tube is fitted at one end with an octagonal clamping head, which firmly secures the specimen to the tube by means of four screws. About one third of the specimen lies inside the brass tube, to the other end of which is soldered a brass block. To another similar clamping head are fixed two rods, which carry smaller blocks at their other end. Each rod rests in two **V**-shaped rollers which roll on the wider of the rectangular surfaces, the rods being held tightly to the rollers by rubber bands. In this way, the rods are constrained to move in one dimension only—parallel to the direction of the magnetostrictive strain—and the friction between the moving parts is very small. (Previous experience has shown that, unless the friction is kept low, serious errors arise.) Two 0·47-mm. dia. steel rollers were placed between the brass blocks, the relevant surfaces having been previously ground and polished, and the blocks were then pressed together by means of rubber bands. Experiment showed that no error was caused by the use of the steel rollers, the forces between the blocks being sufficient to ensure that no translational motion of the rollers took place. To one steel roller was fitted a small plane mirror and to the other was fitted a concave galvanometer mirror, and light was directed from the plane mirror on to the concave mirror, which focused a spot on a scale about 2 m. away.

Manuscript received 8th August, 1951.

Mr. Lee is in the Department of Physics at the University of Nottingham.

The specimen and attached extensometer were suspended vertically inside a solenoid, which had been previously levelled with a plumb line, by a universal joint ensuring the necessary vertical position of the specimen, parallel to the magnetic field. The advantages of this system are : (i) increased magnification due to two rollers ; (ii) almost complete elimination of errors due to bending of the specimen, since this causes the two mirrors to rotate in the opposite sense; (iii) only the central part of the specimen is used ; (iv) relative insensitivity to vibration ; (v) little disturbance by temperature changes, since the effective coefficient of expansion of the specimen is the difference between the coefficients of expansion of the brass and the specimen.

The sensitivity of the system was such that, using a 15-cm. length of specimen, a deflection of 1 mm. on the scale corresponded to a longitudinal strain of 4×10^{-7}. It was thus possible to measure magnetostrictive strains as low as 10^{-7} without difficulty. This sensitivity was sufficient for most purposes, and reproducibility was excellent for most materials—at least to 1%. For a few exceedingly strain-sensitive substances the reproducibility was found to be rather worse, because some stress must be applied to the specimen to transmit its motion to the rollers. Annealed nickel is probably the worst material in that respect, and this must partly account for the differing results obtained by various workers for the magnetostriction of this material. For hard-drawn materials and magnetically hard materials such as cobalt and high coercivity alloys, which are strain-insensitive, the reproducibility was almost perfect.

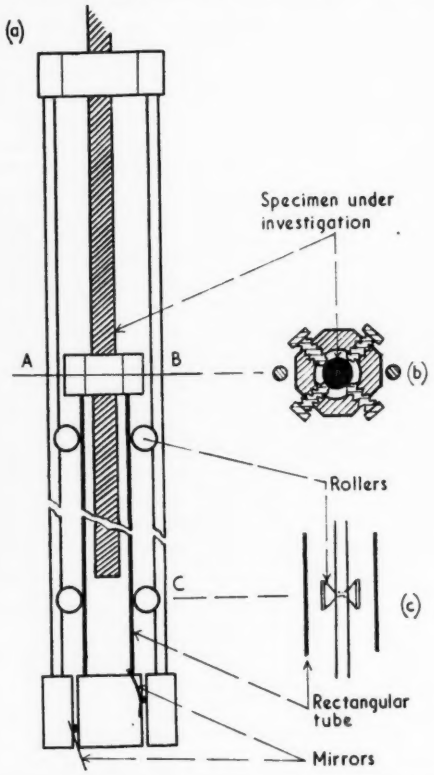


Fig. 1—Diagram of apparatus : (*a*) Front view of extensometer (rectangular tube shown in section) ; (*b*) cross-section at *AB*, showing method of clamping specimen ; (*c*) side view at *C*, showing construction of rollers

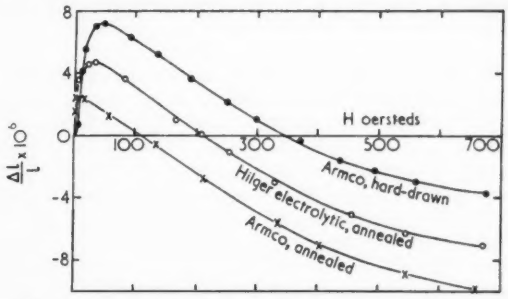


Fig. 2—Magnetostriction of various grades of iron

The magnetic field was supplied by a solenoid, 60 cm. long, wound on a brass water-jacket and capable of producing a field of nearly 700 oersteds when using the town D.C. supply. An auxiliary winding was used to compensate the vertical component of the earth's field. The current was varied by the usual series rheostats. Demagnetization of the specimen was effected by using a Variac transformer, and it was found necessary to tune the solenoid to resonate at 50 cycles/sec., with a 12-μF. condenser in series.

Continuous circulation of water through the cooling jacket of the solenoid proved unsatisfactory, owing to the large temperature fluctuations in the water supply, so the water jacket was used simply to thermally isolate the windings from the centre of the solenoid. Also, the large currents required to produce the greatest fields generated considerable heat ; however, there was a lag of 2–3 min. before the heat affected the specimen, and readings were taken during this period.

DISCUSSION OF RESULTS

Iron

Bates and Harrison[3] investigated the thermal changes in Hilger electrolytic and Armco iron in various states. The virgin curves are shown in Fig. 2, in which the magnetostriction is plotted against the effective field. (In all the remaining figures the magnetic field specified is the true field acting on the

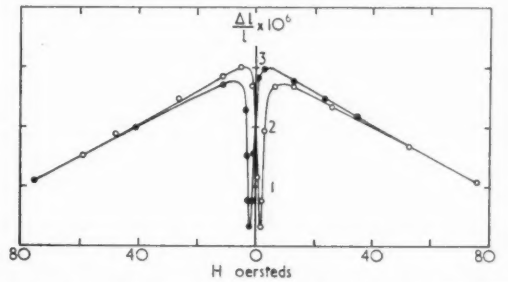


Fig. 3—Magnetostriction of annealed Armco iron during a hysteresis cycle

specimen.) Armco iron had been previously investigated only once, by Brown,[6] who obtained curves of exactly the same shape as those in Fig. 2. The slopes of the final parts of the curve are almost the same for the annealed specimen as for the same specimen in the hard-drawn state, and this confirms the view that in iron the chief anisotropy is magnetocrystallic, the effect of strain anisotropy being very small in comparison. Figure 3 shows the typical behaviour of iron subjected to a normal hysteresis cycle. The maximum elongation in the region $I_{sat} \rightarrow I_{rem}$ is greater than the corresponding maximum in the region $I_{rem} \rightarrow I_{sat}$. The drift of the maximum on the return quarter cycle towards $H = 0$ is caused by irreversible 90° wall movements; these contribute to the initial rise of the curve in fields of 4–10 oersteds, and mask the contraction due to domain vector rotation, which begins in very small fields. In the return quarter cycle there is nothing to mask the effect due to rotations, and the curve continues to rise until $H = 4$ oersteds, when the reversible 90° wall movements begin. The curves in Fig. 3 are typical of all materials for which λ_{100} and λ_{111} have different signs, and the qualitative interpretation of the magnetization curve is thus greatly simplified.

Cobalt

Measurements were made on two cobalt rods whose thermal behaviour had previously been studied by Bates and Edmondson[7] and whose ΔE effect had been investigated by Street.[8] Cobalt is usually a mixture of face-centred and hexagonal structures: in the annealed state, only the hexagonal form is normally present. In hexagonal cobalt there is a single axis of easy magnetization, *i.e.*, the [1000] direction, and magnetization must proceed solely by 180° boundary movements and subsequent rotations against the magnetocrystalline forces. The magnetostriction may therefore be expected to increase steadily with increasing applied field. The behaviours of the two specimens in the unannealed and annealed states are very similar, and this is attributed to the fact that the structure of the two materials is similar, each consisting almost entirely of the hexagonal phase, a conclusion subsequently confirmed by X-ray examination. The relevant virgin curves are shown in Fig. 4.

Alloys

The alloys were supplied in the hard-drawn state and were those used by Bates and Harrison in their investigation of the thermal changes.[3] Their compositions were as follows:

Alloy	Composition, wt.-%						
	Ni	Cu	Fe	C	Si	Mn	S
36% Ni–Fe	36	0·1	Bal	0·05	0·15	0·5	0·005
42% Ni–Fe	42	0·1	Bal	0·05	0·15	0·5	0·005
48% Ni–Fe	48	0·1	Bal	0·05	0·15	0·5	0·005
W5	Bal	0·1	0·4	0·05	4·0	0·6	0·005
W6	Bal	0·1	0·4	0·05	2·5	0·6	0·005
Monel	67·35	30	1·4	0·15	0·1	1·0	0·01
Mangonic	Bal	0·1	0·4	0·05	0·1	3·0	0·005

The effect of cold-drawing on the magnetic properties is determined very largely by the magnetostriction of the material concerned, becoming greater as the magnetostriction increases. Normally, the effect is to make the specimen magnetically hard, so that

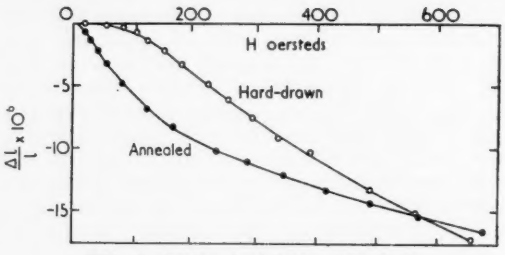


Fig. 4—Magnetostriction of cobalt

very considerable fields have to be applied to produce saturation. This disadvantage is offset by the fact that, in some cases (*e.g.*, nickel), this treatment produces a perfectly random domain distribution in the demagnetized state, owing to the random distribution of internal stresses set up in the material.

Nickel–Iron Alloys—The results obtained for these alloys are shown in Fig. 5. The virgin curves are similar to those obtained by other workers[9, 10] for the corresponding annealed materials, and one can only assume that the mechanical treatment to which they had been subjected was not very severe. For 36% Ni–Fe the Curie temperature is fairly low, and the linear increase of magnetostriction in high fields is attributable to changes in the spontaneous magnetization and magnetostriction (Becker and Döring's 'erzwungene Magnetostriktion'[1]).

An interesting feature is the anomalous behaviour of this alloy when subjected to an alternating field. The hysteresis is very small indeed, and the ascending and descending branches of the curve cross not only at $H = 0$ but also at $H = 20$ oersteds (*see* Fig. 6). In fields greater than 20 oersteds the descending branch of the curve always lies beneath the ascending branch. Magnetic processes are known to be reversible in this region—in any case, any irreversibility would cause the descending branch to lie above the ascending one. The Curie temperature of this alloy is low, about 270° C., and in high fields large changes in spontaneous magnetization may occur; this gives rise to the very large thermal changes observed by Bates and Harrison, as a result of the ordinary magneto-caloric effect. The necessity for rapid measurement of magnetostriction in high fields, to avoid spurious effects caused by the temperature rise of the solenoid, has already been mentioned (p. 161). The field changes are thus made almost adiabatically, so that the observed increase in length is caused mainly by magnetostriction but partly by thermal

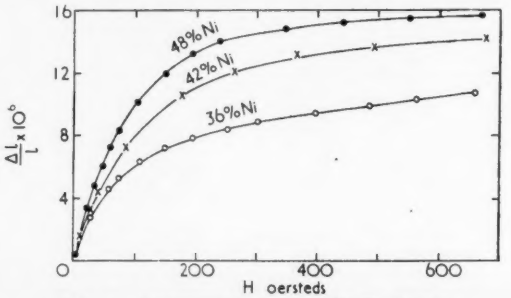


Fig. 5—Magnetostriction of Ni–Fe alloys

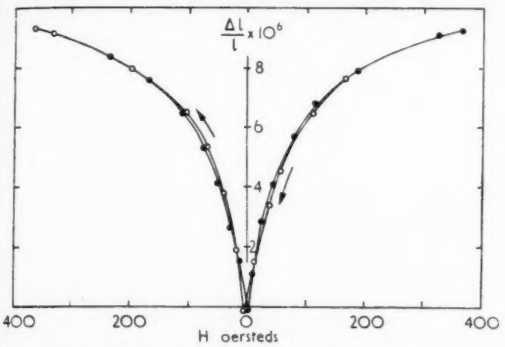


Fig. 6—Magnetostriction of 36% Ni–Fe alloy during a hysteresis cycle

expansion of the material, the rise in temperature being due to the ordinary magneto-caloric effect. Part of the heat generated is communicated to the surroundings between successive field changes, and this accounts for the apparent hysteresis. For the 36% Ni–Fe alloy the effect is found only in fairly large fields; a cycle whose maximum field was 47 oersteds showed no such effect. The fact that the coefficient of expansion of this alloy is very small (of the order of 2×10^{-6}/°C. at room temperature) implies that a similar effect may occur in all materials. This effect is not usually observed, probably because it is masked by the ordinary hysteresis effect and, in any case, would be indistinguishable from the latter if the magnetostriction were negative.

The values of the magnetostriction of these alloys are much lower than those previously reported. This may result from non-randomness in the domain vector distribution in the demagnetized state caused by cold-drawing.

W5 and W6—These Ni–Si alloys contain 4% and 2·5% of Si, respectively. The effect of adding silicon is to lower the Curie temperature, and the Curie point of W5 is approximately 30° C. (*see*, for example, Bates and Davis[11]). At room temperature it was impossible to make more than a rough estimate of the magnetostriction, owing to its very large magneto-caloric effect; however, the magnetostriction of W5 is not greater than 10^{-7}. The behaviour of W6 is characteristic of a material with quasi-isotropic magnetostriction, and is very similar to that of nickel (*see* Fig. 7).

Monel Metal—The addition of copper to nickel produces a lowering of the Curie temperature and

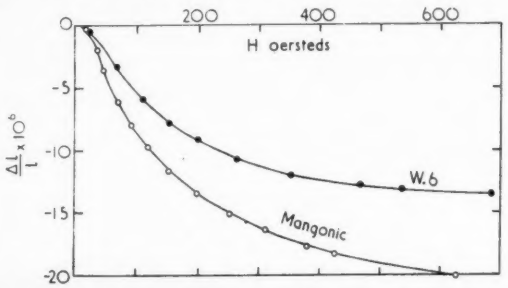


Fig. 7—Magnetostriction of W6 and Mangonic

the saturation moment. The Curie point of a 30% Cu–Ni alloy is stated to be 25° C. The magnetostriction at room temperature was too small to be detected, even with a more sensitive form of the apparatus, and must have been less than 10^{-8}.

Mangonic—The behaviour of this alloy is shown in Fig. 7, in which the results (and those for W6) are plotted against applied field. No correction is made for demagnetization effects, which are important only in magnetically soft materials exhibiting a large remanence, *e.g.*, iron. The properties of Mangonic are very similar to those of W6.

Nickel–Cobalt Alloys—These were obtained in the form of bars, and were cut and ground into rods 40 cm. long × 6 mm. dia. The rods were annealed by heating *in vacuo* to 1000° C. and cooling at the rate of about 100° C./hr. Their compositions by weight were as follows:

	C, %	Si, %	Fe, %	Mn, %	Ti, %	Ni, %	Co, %
I	0·01	0·06	0·06	Trace	Nil	90·2	Bal
K	0·01	0·06	0·10	0·01	Nil	71·0	Bal
L	0·01	0·06	0·12	Trace	0·01	62·4	Bal
M	0·02	0·07	0·21	0·03	0·07	50·7	Bal
N	0·02	0·06	0·22	0·02	0·07	41·1	Bal
O	0·01	0·08	0·36	0·03	0·07	31·1	Bal
P	0·01	0·09	0·37	0·07	Nil	21·7	Bal
Q	0·01	0·12	0·54	0·11	Nil	10·53	Bal

Graphs of the magnetostrictive behaviour of these alloys are shown in Fig. 8. The phase change at about 75% Co is clearly marked. Alloys containing more than this amount of cobalt possess hexagonal structures, and the magnetostrictions of alloys in this range are similar to that of annealed cobalt. Addition of nickel to cobalt decreases the lattice spacing (pure cobalt has parameters $a = 2{\cdot}502$ Å., $c/a = 1{\cdot}6233$, whereas an 80% Co alloy has parameters $a = 2{\cdot}489$ Å., $c/a = 1{\cdot}621$) and reduces the magnetostriction from about 40×10^{-6} to zero at about 76% Co. Unfortunately, owing to the large magnetocrystalline energy of alloys in this region, it was not possible to produce saturation in specimens *P* and *Q*. Alloys containing more than 30% of Ni are face-centred cubic, and those containing 50–70% of Ni have magnetostriction properties almost identical with that of cubic cobalt. According to Shih,[12] the direction of easy magnetization for the cubic phase is [111] for 0–5% Co and also for 20–60% Co. In the region 5–20% Co the [100] is the easy direction, and the magnetostriction shows a change, λ_{100} changing its sign from negative at 10% Co to positive at 30% Co. The curves corresponding to the range 30–70% Co show a contraction in small fields followed by an expansion in high fields, due to domain rotations. Since [111] is the direction of easy magnetization, the initial part, due to boundary movement, is governed solely by the magnetrostriction coefficient in the [111] direction. In high fields both λ_{111} and λ_{100} are operative, and the increasing steepness of the high-field part of the curves may be attributed to an increase in the magnitude of λ_{100}, which must also be positive; λ_{111} is always negative and probably varies only slightly with composition.

Temperature Coefficients

Stoner and Rhodes[4] pointed out that if, in addition to the normal crystalline anistropy, there exists aniso-

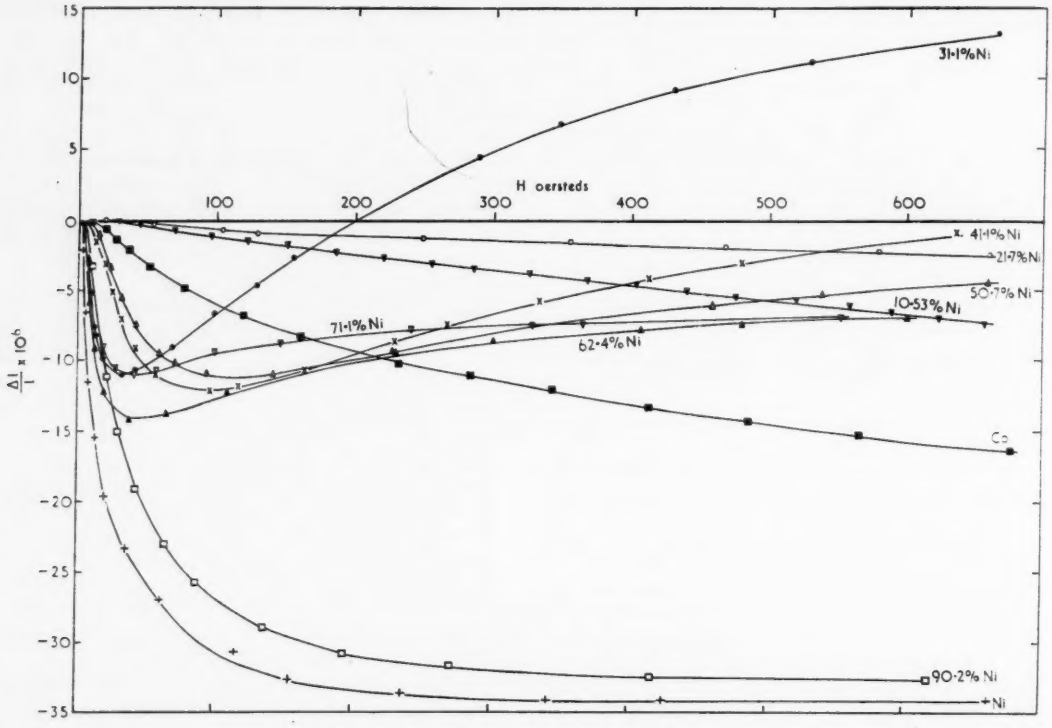


Fig. 8—Magnetostriction of Ni–Co alloys.

tropy due to strain, then, to estimate the effect of the strain anisotropy on the thermal changes, not only the magnetostriction but also its temperature coefficient must be known. Measurements of magnetostriction as a function of temperature present considerable difficulty, and few attempts have been made[13–15]. A further difficulty in the present experiments arose because the drawing treatment rendered many of the alloys difficult to saturate. Since the maximum available field was about 700 oersteds, it is certain that some of these alloys (particularly W6 and Mangonic) were not fully saturated. It was decided, therefore, to assume that the measured magnetostriction in a large field (approx. 700 oersteds) only differed from the true saturation value by a constant factor, independent of the temperature. For most of the alloys this constant was probably about 0·95, so that the values of $d\lambda/dT$ for those alloys which are difficult to saturate (*i.e.*, W6 and Mangonic) may be too small by about 5%.

The temperature of the specimen was varied by circulating warm or cooled water through the solenoid water-jacket. Using a large reservoir of high thermal capacity it was possible to maintain steady temperatures between 5° and 30° C. The temperature of the specimen was measured by a calibrated thermocouple.

Over such a small temperature range the magnetostriction of all these alloys decreased linearly with temperature. Values obtained for the change in λ per °C. were : Mangonic, 3×10^{-8} ; W6, 9×10^{-8} ; 36% Ni–Fe, $-4{\cdot}5 \times 10^{-8}$; 42% Ni–Fe, $-2{\cdot}5 \times 10^{-8}$; all measured at 2·0° C. The large value of $d\lambda/dT$ for W6 is consistent with its low Curie temperature.

Acknowledgments

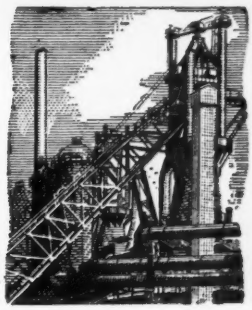
The author wishes to thank Professor L. F. Bates, F.R.S., who directed this research, for his constant guidance and encouragement throughout. Thanks are also due to Mr. H. W. G. Hignett, Research and Development Department of the Mond Nickel Co., for supplying the Ni–Co alloys.

References

1. R. Becker and W. Döring : " Ferromagnetismus." Berlin, 1939 : Julius Springer.
2. L. F. Bates and J. C. Weston : *Proc. Phys. Soc.*, 1941, vol. 53, pp. 5–33.
3. L. F. Bates and E. G. Harrison : *Ibid.*, 1948, vol. 60, pp. 213–235.
4. E. C. Stoner and P. Rhodes : *Phil. Mag.*, 1949, vol. 40, pp. 481–521.
5. H. Nagaoka : *Ibid.*, 1894, vol. 37, p. 131.
6. W. F. Brown, Jr. : *Phys. Rev.*, 1936, vol. 50, pp. 1165–1172.
7. L. F. Bates and A. S. Edmondson : *Proc. Phys. Soc.*, 1947, vol. 59, pp. 329–343.
8. R. Street : *Ibid.*, 1948, vol. 60, pp. 236–243.
9. A. Schulze : *Zeitschrift für Physik*, 1928, vol. 50, pp. 448–505.
10. K. Honda and K. Kido : *Sci. Rep. Res. Inst., Tôhoku Univ.*, 1920, vol. 9, pp. 221–231.
11. L. F. Bates and J. H. Davis : *Proc. Phys. Soc.*, 1948, vol. 60, p. 307.
12. J. W. Shih : *Phys. Rev.*, 1936, vol. 50, pp. 376–379.
13. W. Döring : *Zeitschrift für Physik*, 1936, vol. 103, pp. 560–582.
14. H. Takaki : *Ibid.*, 1937, vol. 105, pp. 92–103.
15. D. Kirkham : *Phys. Rev.*, 1937, vol. 52, pp. 1162–1167.

B. I. S. R. A.

BRITISH IRON AND STEEL RESEARCH ASSOCIATION



The Thermodynamics of Substances of Interest in Iron and Steel Making

By F. D. Richardson and J. H. E. Jeffes

III—SULPHIDES

SYNOPSIS

A survey is made of the available data on the thermodynamics of sulphides and of gaseous sulphur compounds of interest in iron and steel making. The results are plotted on free-energy/temperature diagrams, and equations and likely accuracies are quoted for each substance.

THERMODYNAMIC data available for oxides and the compounds between them were reviewed in Parts I and II.[49, 50]

In the present paper equilibrium and thermal data have been employed in deriving the free-energy equations for sulphides. The data are presented in the form of the now familiar ΔG°–T diagrams. The sources of the data are indicated and likely accuracies have been proposed.

The heat capacity and entropy data calculated by Kelley[27, 28] have been found invaluable, and have been used without recalculation. The data from the Bulletin on sulphides[26] have been checked, and corrected where necessary.

The use of the free-energy diagrams for rapid and approximate calculations has already been explained in Part I.[49]

FREE-ENERGY/TEMPERATURE DIAGRAMS

Standard States—The standard states selected for the various substances are as follows :

Sulphur—diatomic sulphur gas
Sulphides—pure stable solids or liquids according to whether they are above or below their melting points
Gases—one atmosphere pressure
Metals—pure stable solids, liquids, or gases according to whether they are above or below melting or boiling points.

Linearity—All the recommended free-energy equations are linear, and the free-energy values given by the linear equations are well within the likely limits of error, although neither ΔH° nor ΔS° is necessarily constant within these same limits.[49]

Gaseous Sulphides and Sulphur

Figure 1 is the free-energy diagram for the gaseous sulphides that are likely to be of interest in furnace atmospheres or laboratory investigations. Values of the dissociation constants (K_D) for these gases, according to the equations indicated, can be read directly from the right-hand logarithmic scale. If, for example, the constant is required for the dissociation $2COS = 2CO + S_2$, at 1000° C., a ruler (preferably transparent), or alternatively a fine string, should be laid on the diagram so that one edge passes through the COS line at 1000° C., and also through the point D on the left-hand side of the diagram. The point at which this edge cuts the dissociation constant scale ($10^{0.33}$, *i.e.*, 2·14) gives the value of K_D, interpolation between the markings being logarithmic. This value is also the pressure of diatomic sulphur gas in atmospheres, in equilibrium with 1 atm. pressure of each of the other two gases.

From the H_2S/H_2 scale on the right-hand edge of the diagram, it is possible to read directly the ratio of H_2S/H_2 in equilibrium with the gas systems represented by the different free-energy lines. For example, the H_2S/H_2 ratio that could be in equilibrium with 1 atm. of CO and 1 atm. of COS (or, in this case, with any pressures of CO and COS, provided that they are equal) at 1200° C. can be obtained from the diagram. As described for reading S_2 pressures, a transparent ruler can be used, its edge, in this case, passing through the point H on the left-hand side of the diagram, and through the point at which the CO–S_2–COS line

Paper CP/10/7 of the Chemistry Department of the British Iron and Steel Research Association, received 30th January, 1952.

Dr. Richardson is Director of the Nuffield Research Group in Extraction Metallurgy at the Royal School of Mines. Mr. Jeffes was until recently in the Chemistry Department of the British Iron and Steel Research Association.

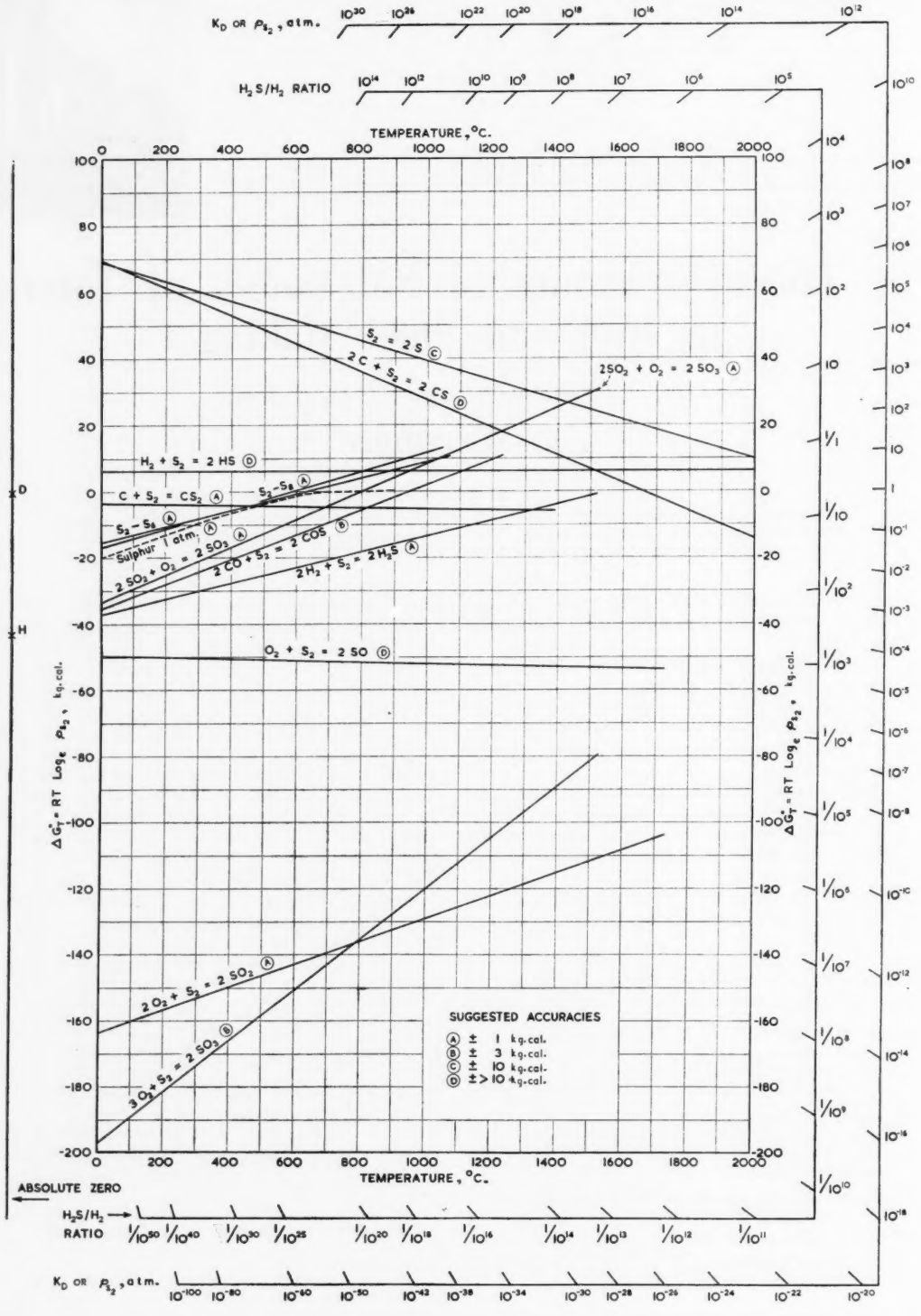

K_D OR P_{S_2}, atm.
H_2S/H_2 RATIO
TEMPERATURE, °C.
$S_2 = 2S$ (C)
$2C + S_2 = 2CS$ (D)
$2SO_2 + O_2 = 2SO_3$ (A)
$H_2 + S_2 = 2HS$ (D)
$C + S_2 = CS_2$ (A)
$S_2 - S_8$ (A)
Sulphur 1 atm.
$2SO_2 + O_2 = 2SO_3$ (A)
$2CO + S_2 = 2COS$ (B)
$2H_2 + S_2 = 2H_2S$ (A)
$O_2 + S_2 = 2SO$ (D)
$2O_2 + S_2 = 2SO_2$ (A)
$3O_2 + S_2 = 2SO_3$ (B)
$\Delta G^\circ_T = RT \log_e P_{S_2}$, kg.cal.
SUGGESTED ACCURACIES
(A) ± 1 kg.cal.
(B) ± 3 kg.cal.
(C) ± 10 kg.cal.
(D) ± > 10 kg.cal.
ABSOLUTE ZERO
H_2S/H_2 RATIO
K_D OR P_{S_2}, atm.

Fig. 1—Free-energy diagram for gaseous sulphides

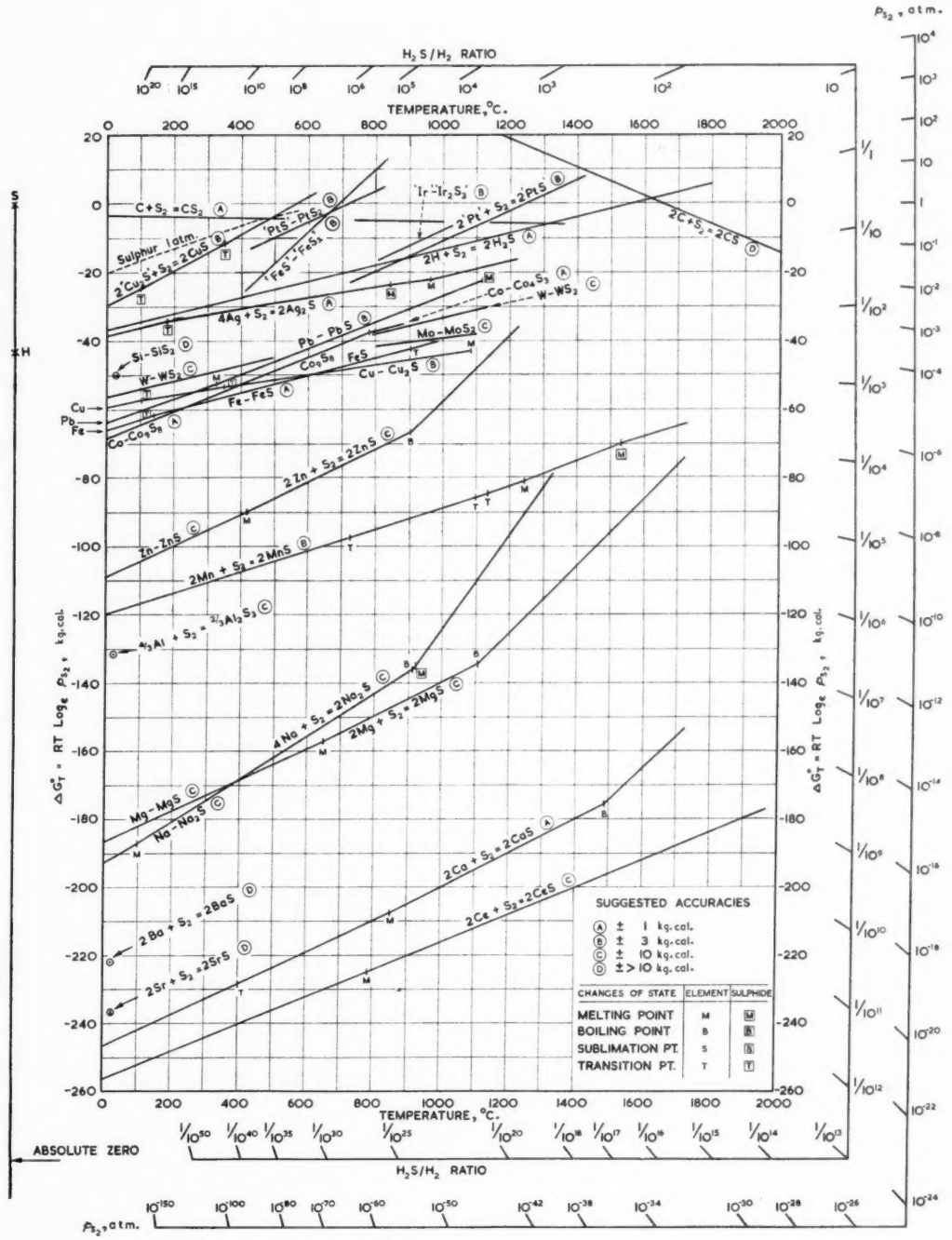


Fig. 2—Free-energy diagram for sulphides of metals

intersects the 1200° C. temperature line. The point at which the ruler edge cuts the H_2S/H_2 ratio scale on the right-hand side of the diagram gives the equilibrium H_2S/H_2 ratio (in this case, $10^{1.32}$, *i.e.*, 20·7). As in the case of the sulphur pressure scale, interpolation between markings on this scale must be logarithmic. A fuller explanation of the use of such scales is to be found in Part I.[49]

The dotted curve in Fig. 1 represents the S_2 potentials of sulphur in its stable form at 1 atm. pressure. This is taken as rhombic sulphur* below its natural melting point of 110·4° C. Between this temperature and 444·6° C. (the natural boiling point), the stable form is the equilibrium liquid consisting of S_λ and S_μ. Above the boiling point, it is a mixture of S_8, S_6, and S_2 molecules, consisting almost entirely of S_2 molecules above 850° C.

The species HS, and particularly CS, cannot at present be neglected with safety in any thermodynamic calculations on systems involving sulphur-containing gases at high temperatures. Hitherto, it has been assumed that the concentration of CS or HS is insignificant in comparison with H_2S, COS, CS_2, etc.

The accuracy of the available data is inadequate for an exact calculation of the proportions of sulphur existing as HS or CS in any equilibrium gas mixture. It is thus impossible to calculate accurately the sulphur potential of a gas mixture from the overall gas composition, and high-temperature work on sulphur in metal and slag systems is hampered thereby. For example, the extent to which carbon is believed to raise the activity coefficient of sulphur in liquid iron may be incorrect, owing to the existence of CS. This effect of carbon has been studied by measuring the concentration of sulphur in liquid iron (both with and without carbon) after it has been brought into equilibrium with a gas mixture of hydrogen sulphide and hydrogen, which is passed through or over the metal. Any formation of CS by the carbon in the melt would lower the concentration of H_2S in contact with the melt. The sulphur potential of the gas would therefore be lower than that which would be obtained from the same gas mixture in the absence of carbon. An investigation has therefore been started by one of the authors (F.D.R.) in an attempt to determine the importance of CS.

Sulphides of the Metals

Figure 2 is the free-energy diagram for sulphides of the metals. It is similar to Fig. 1, and can be used in the same way. A number of metals which are not of direct interest in iron and steel making, such as platinum, iridium, and molybdenum have been included, because their behaviour limits their use as containers and heating elements in laboratory investigations of sulphide systems.

The entropy changes accompanying the formation of the sulphides shown in Fig. 2 and of the oxides shown in Fig. 1 of Part I are similar. The patterns of slopes in the two figures are much the same, the relationships between the curves for CS, CS_2, H_2S and the solid and liquid sulphides corresponding to those between CO, CO_2, H_2O, and the condensed oxides. Reduction of metallic sulphides by carbon or hydrogen is usually ineffective, whereas that of oxides is not, because of the relatively small stabilities of CS, CS_2, and H_2S. Generally, if sulphides are to be completely reduced in pyrometallurgical operations, they must first be converted to oxides and then to the metal. With the less stable oxides (*e.g.*, lead and copper), it is, however, possible to reduce the sulphide directly to the metal with oxygen, provided that the oxygen is supplied at a sufficiently low potential. This is due to the *great* stability of SO_2 relative to oxygen and sulphur vapour.

NON-STOICHIOMETRY OF METAL SULPHIDES

Many metal sulphides, including those of iron, are non-stoichiometric. In the case of iron, they may be approximately represented by the formulae 'FeS' and 'FeS_2,' but the precise proportions of iron to sulphur are dependent on the sulphur potential or sulphur pressure above them. In the presence of two phases, 'FeS' and 'FeS_2,' the sulphur potential ($\Delta\mu_{S_2}$) is, of course, dependent only on temperature, as it is for two normal stoichiometric phases such as Mg and MgS. The precise compositions of the equilibrium 'FeS' and 'FeS_2' phases are thus also dependent on temperature, and can be read from the phase diagram

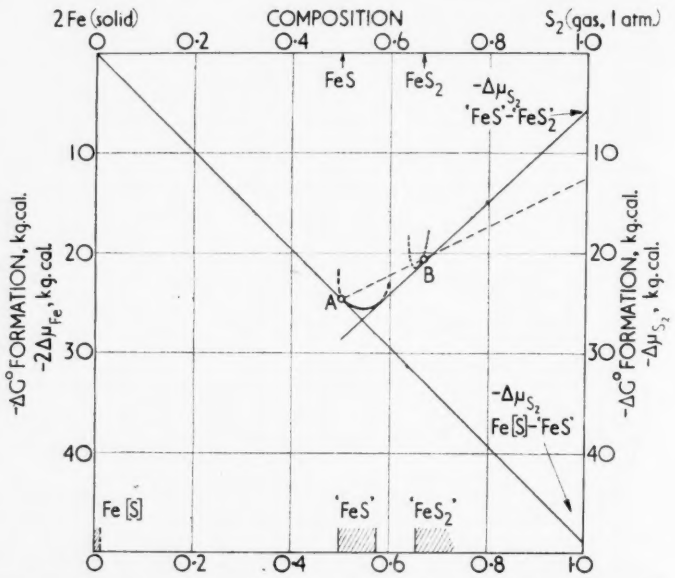


Fig. 3—Approximate representation of free energies of forming equilibrium mixtures of Fe and S at 900° K. from solid iron and diatomic sulphur gas at 1 atm.

* The monoclinic form, stable between 95° C. and its natural melting point of 114·6° C., has been neglected.

where it has been established. At 627° C., for example, they are approx. $FeS_{1\cdot35}$ and $FeS_{1\cdot9}$.[19] A number of the free-energy curves shown in Fig. 2 have been derived from measurements of the sulphur potentials in equilibrium with two phases, of which one, and sometimes both, are non-stoichiometric sulphides. In such cases, the formulae of the sulphides are given in inverted commas. The curves then give the free-energy changes associated with reactions of the type,

$$aM_xS_y + S_2 = bM_cS_d \quad \ldots\ldots(1)$$
$$wM + S_2 = M_xS_y \quad \ldots\ldots(2)$$

where M and S represent metal and sulphur atoms, and a, b, w, etc., are numbers, which may be fractional.

Where heats of formation, entropies, and heat capacities have been measured for sulphides exhibiting non-stoichiometry, the investigators have generally worked at one composition only in each composition range. Where stoichiometric sulphides can be made, these have usually been selected. The free energies of formation calculated from such thermal data are different from those derived from the equilibrium measurements. In the stoichiometric cases, the changes apply to the reactions,

$$2MS + S_2 = 2MS_2 \quad \ldots\ldots(3)$$
$$\text{and } 2M + S_2 = 2MS \quad \ldots\ldots(4)$$

The relation between the two types of data can be seen from Fig. 3, which is a plot of the free energy of formation of 2 g.atoms of an equilibrium mixture of iron and sulphur at 900° K. Figure 3 is based on the data cited in the Appendix, but is not very accurate owing to the lack of knowledge of the composition limits of 'FeS' and 'FeS_2,' and of the solubility of sulphur in solid iron. The point A has been derived from the Fe–FeS equilibrium, because it appears that FeS is stoichiometric (or almost so) when in equilibrium with iron. The point B has been calculated from thermal data on FeS_2 of nearly stoichiometric composition. Measurements of p_{S_2} in equilibrium with the system 'FeS'–'FeS_2' have shown that $\Delta\mu_{S_2}$ is $-5{\cdot}7$ kg.cal. at 900° K., the two phases having the compositions $FeS_{1\cdot35}$ and $FeS_{1\cdot9}$. The tangent to the curves for 'FeS' and 'FeS_2' therefore cuts the free-energy axis (sulphur side) at $-5{\cdot}7$. If the two *stoichiometric* phases could be in equilibrium together, $\Delta\mu_{S_2}$ would be $-12{,}400$ cal., as indicated by the intercept made on the free-energy axis (sulphur side) by the line through the points A and B. The tangent to the curves for Fe[S] and 'FeS' cuts this same free-energy axis at $-49{\cdot}2$ kg.cal., which is the sulphur potential in equilibrium with these two phases.

Acknowledgments

The authors are indebted to Dr. J. Pearson and Dr. O. Kubaschewski for their helpful criticism and to Mrs. U. Ende for assistance in the collection of data on which the calculations are based. Great use has been made of the various Bulletins of the U.S. Bureau of Mines, entitled "Contributions to the Data on Theoretical Metallurgy" and prepared by K. K. Kelley.

APPENDIX

The appendix is divided into two parts. The first is devoted to the gaseous compounds of sulphur, and the second to the metallic sulphides. Where no reference is made to data obviously essential to the derivation of the equations recommended, they are to be found in the appendices either of this paper or of Part I.[49]

The derived equations give the standard free energies of reaction (ΔG°) in calories for the reactions *as written* in gram molar quantities.

As in Parts I and II, the accuracies have been estimated and each equation has been graded into one of the following classes:

A	± 1	C	± 10
B	± 3	D	$\pm > 10$

The limits proposed for each class are the limits within which the true values of ΔG° almost certainly lie (probability, say, 95%). The limits take into account the spread of the data selected as most reliable, the extent to which they may be extrapolated, and the opinion of the authors concerning the likely accuracies of the techniques employed and the reliability of the various investigators. The authors therefore wish to stress that the gradings have no precise statistical significance.

The accuracy grading, which is set after each chemical equation, normally applies to all the free-energy equations immediately following. In cases where the accuracy changes with temperature, the appropriate gradings have been added after the free-energy equations.

GASEOUS COMPOUNDS OF SULPHUR

Sulphur

$(S_2 = 2S_{\text{rhombic}})$ Accuracy A

$$\Delta H^\circ_{298^\circ\text{K.}} = -31{,}020$$

In many of the calculations on the metal sulphides, it was necessary to convert heats of formation from rhombic sulphur to those from S_2. The value of $\Delta H^\circ_{298^\circ\text{K.}}$ used for this purpose is that evaluated by Kelley.[26] It is 230 cal. more negative than that now recommended by the Bureau of Standards.[38] This difference is well within the error limits of the metal sulphide data used in this paper.

(S_2 = Sulphur — stable form at 1 atm.)

The dotted curves in Figs. 1 and 2 represent the S_2 potentials (ΔG°) of rhombic sulphur below its natural melting point (110·4° C.), of liquid sulphur $S_{\lambda,\mu}$ between this temperature and the natural boiling point (444·6° C.), and of sulphur vapour at 1 atm. total pressure ($S_2 + S_8 + S_6$) above the boiling point.

The necessary values were obtained as follows:

Temp., °C.	S_2 Potential, cal.	
25	$-19{,}360$	Kelley[26]
110	$-16{,}010$	From the calculations of Preuner and Schupp[45] on the equilibrium between liquid sulphur and S_8, and the present authors' equation for the S_2–S_8 equilibrium
200	$-12{,}830$	
300	-9500	
400	-6220	
450	-4610	
600	-1210	From present authors' equations for the S_2–S_8 and S_2–S_6 equilibria
640	-570	
700	-100	
850	0	

$(S_2 = \frac{1}{4}S_8)$ Accuracy A

$$\Delta G^\circ_{298\text{–}1300^\circ\text{K.}} = -24{,}800 + 28{\cdot}29T$$

$(S_2 = \frac{1}{3}S_6)$ Accuracy A

$$\Delta G^\circ_{298\text{–}1300^\circ\text{K.}} = -22{,}150 + 24{\cdot}58T$$

The above equations are based directly on the experimental results of Preuner and Schupp,[45] who measured the densities of gaseous sulphur at temperatures between 200° and 1020° C. The calculations of Kelley[26] on these equilibria are in error.

$$(S_2 = 2S) \qquad \text{Accuracy } C$$
$$\Delta G^\circ_{298\text{-}2200^\circ\text{K.}} = +77{,}250 - 29{\cdot}70T$$

The dissociation of diatomic sulphur into atoms has been studied by Nernst[39] and von Wartenberg,[63] who determined the mean molecular weight of sulphur gas at about 2000° C. Their results show that at 2050° C. the molecular weight lies between 50 and 54, at a total sulphur pressure of 0·5–1·0 atm. These figures give values of 5·0–12·1 kg.cal. for ΔG° for the dissociation of a mole of S_2.

According to Gaydon,[14] spectroscopic measurements indicate that the dissociation energy of S_2 into normal atoms (*i.e.*, his D° which is equal to our ΔH°_0) is most probably 101 ± 3 kg.cal., although 83 and 76 kg.cal. are also possible values. The results of Nernst and von Wartenberg agree with the lowest value, for, when this is coupled with the available heat capacity and entropy data for S_2 and S,[38, 27] $\Delta G^\circ_{2323^\circ\text{K.}}$ becomes 11·2 ± 3 kg.cal.

The equation recommended is based on $\Delta G^\circ_{2323^\circ\text{K.}} = 8{\cdot}6$ kg.cal., and a temperature dependence of ΔG° equal to that calculated for the range 1500–2500° K. (*i.e.*, the range of interest for the dissociation and the formation of CS, HS, etc.) from the entropy and heat-capacity data. The value of 8·6 kg.cal. for $\Delta G^\circ_{2323^\circ\text{K.}}$ leads to a value of 73 kg.cal. for ΔH°_0. This is taken as the most probable value for the calculations on CS, HS, and SO.

Sulphur Monoxide

$$(O_2 + S_2 = 2SO) \qquad \text{Accuracy } D$$
$$\Delta G^\circ_{298\text{-}2000^\circ\text{K.}} = -49{,}000 - 2{\cdot}5T$$

According to Gaydon,[14] the dissociation energy of SO into normal atoms is either 119·5 or 92·3 kg.cal., the higher value being preferred. When this higher value is coupled with the most probable value for the dissociation energy of S_2 (73 kg.cal.), the dissociation energy of oxygen, 117·2 kg.cal.,[14] and the available heat-capacity data for SO, O_2, and S_2,[38] the equation recommended above is derived. The error limits are large because the lower value for the dissociation energy of SO would lead to a value of + 6 kg.cal. for the temperature-independent term in the equation.

Sulphur Dioxide

$$(2O_2 + S_2 = 2SO_2) \qquad \text{Accuracy } A$$
$$\Delta G^\circ_{298\text{-}2000^\circ\text{K.}} = -173{,}240 + 34{\cdot}62T$$

The equation is a very close linear approximation to that derived by Kelley[26] from thermal and spectroscopic data. It agrees closely with the calculations of Brewer[47] (*loc. cit.*, p. 65).

Sulphur Trioxide

$$(O_2 + 2SO_2 = 2SO_3) \qquad \text{Accuracy } A$$
$$\Delta G^\circ_{318\text{-}1800^\circ\text{K.}} = -45{,}200 + 42{\cdot}72T$$
$$(3O_2 + S_2 = 2SO_3) \qquad \text{Accuracy } B$$
$$\Delta G^\circ_{318\text{-}1800^\circ\text{K.}} = -218{,}440 + 77{\cdot}34T$$

The equilibrium between SO_2, O_2, and SO_3 has been measured from 801 to 1170° K. by Bodenstein and Pohl,[7] and from 933 to 945° K. by Taylor and Lehner.[60] When plotted, their experimental results agree very closely, and lead to the linear equation recommended above. The entropy change accompanying this reaction at 1000° K., calculated from the entropy data available for all three gas molecules, is 42·7 ± 2·5 cal./degree. This is good confirmation of the equation. The second equation has been derived directly from the first *via* the equation given for sulphur dioxide.

Hydrogen Monosulphide

$$(H_2 + S_2 = 2HS) \qquad \text{Accuracy } D$$
$$\Delta G^\circ_{298\text{-}2200^\circ\text{K.}} = +6000 - 0{\cdot}0T$$

The energy of dissociation of HS into normal atoms is probably 85 ± 4 kg.cal.[42] When this value is combined with the energy of dissociation of hydrogen, 103·2 kg.cal.,[14] and the value recommended above for the dissociation of S_2, 73 kg.cal., then ΔH°_0 for the reaction $H_2 + S_2 = 2HS$ becomes + 6 kg.cal. This leads to the equation recommended, if it is assumed that the entropy of formation of HS from H_2 and S_2 is approx. zero. This equation leads to ratios of HS/H_2S in the presence of 1 atm. of H_2, of 3×10^{-5} at 800° K., and 0·3 at 1830° K.

Hydrogen Sulphide

$$(2H_2 + S_2 = 2H_2S) \qquad \text{Accuracy } A$$
$$\Delta G^\circ_{298\text{-}1800^\circ\text{K.}} = -43{,}160 + 23{\cdot}61T$$

The equation is based on the equilibrium data of Preuner,[43] Preuner and Schupp,[46] and Randall and von Bichowsky.[48] There is good agreement between them all.

Carbon Monosulphide

$$(2C_{\text{graphite}} + S_2 = 2CS) \qquad \text{Accuracy } D$$
$$\Delta G^\circ_{298\text{-}2200^\circ\text{K.}} = +81{,}000 - 42T$$

Spectroscopic measurements[14] lead to an energy of 166 ± 23 kg.cal. for the dissociation of CS into normal atoms. When coupled with the heat of vaporization of graphite[38] and the value recommended in this paper for the dissociation of S_2 into normal atoms (+ 73 kg.cal.), this figure leads to a value of + 81 ± 46 kg.cal. for ΔH°_0 for the reaction $2C_{\text{graphite}} + S_2 = 2CS$. If the entropy of formation of 2CS is taken as equal to that of 2CO, the above approximate free-energy equation is obtained.

Lewis and Lacey[35] have made an approximate measurement at 575° K. of an equilibrium which appears to be $CS_{2(g)} = CS_{(g)} + S_{(liq.)}$. This leads to a value of + 7·8 kg.cal. for $\Delta G^\circ_{575^\circ\text{K.}}$ for the reaction $2C_{(graphite)} + S_2 = 2CS$, corresponding to the equation $\Delta G^\circ = +32{,}000 - 42T$. This, however, is probably incorrect. Similar experiments by Lewis and Lacey gave erroneous values for the equilibrium constants for the reactions $2COS = CO_2 + CS_2$ and $2CO + S_{(liq.)} = 2COS$ at 575° K.: 200 and 0·009, instead of 530 and 0·06 respectively. Also, their equation leads to a ratio of CS/H_2S of 400 : 1 at 1800° K. in $H_2/H_2S/CS$ gas mixtures in equilibrium with graphite and 1 atm. of H_2. Although a significant ratio of CS/H_2S under such conditions might be

possible (the recommended equation leads to a ratio of 1 : 1·6), work on the equilibrium between sulphur in liquid iron and H_2/H_2S gas mixtures in the presence and absence of carbon[55, 37, 30] indicates that such a high ratio is very improbable.

The spectroscopic dissociation energy of CS has therefore been taken as the basis for the recommended approximate free-energy equation, which has been graded Accuracy *D*.

Carbon Disulphide

$$(C_{(\beta\ \text{graphite})} + S_2 = CS_2) \qquad \text{Accuracy } A$$
$$\Delta G^\circ_{298\text{–}1600^\circ\text{K.}} = -3100 - 1{\cdot}73T$$

This equation is a linear approximation of that recommended by Kelley,[26] and is thus based on both spectroscopic and gas equilibrium measurements. It agrees with the similar calculations of Brewer[47] (p. 65).

Carbonyl Sulphide

$$(2CO + S_2 = 2COS) \qquad \text{Accuracy } B$$
$$\Delta G^\circ_{298\text{–}1500^\circ\text{K.}} = -45{,}720 + 37{\cdot}40T$$

This equation is based on the calculations of Brewer[47] (p. 65), which are founded on spectroscopic data and measurements of the equilibrium $CO_2 + H_2S = COS + H_2$. The equation agrees with that calculated by Kelley[26] at 600° K., but gives values 2 kg.cal. more positive at 1500° K.

SULPHIDES OF METALS

Aluminium

$$(\tfrac{4}{3}Al + S_2 = \tfrac{2}{3}Al_2S_3) \qquad \text{Accuracy } C$$
$$\Delta G^\circ_{298^\circ\text{K.}} = -131{,}500$$

The heat of formation of Al_2S_3 from rhombic sulphur has been measured by Korshunov[32] and by Kapustinskii and Golutvin,[20] who obtained values of − 121,600 and − 173,000 cal. respectively at 298° K. Both measurements were made by bomb calorimetry: the latter workers attribute the lower value of Korshunov to incomplete combination of sulphur with the metal. Sabatier[54] measured the heat of hydrolysis of Al_2S_3 to gelatinous $Al(OH)_3$. His measurement, when combined with modern heat data and with the heat of hydration of alumina (Klever[31]), leads to an approximate value of − 147 kg.cal. for the heat of formation from rhombic sulphur. The value of Kapustinskii and Golutvin for the heat of formation of Al_2S_3 was accepted, and it was assumed that the entropy of formation of Al_2S_3 from S_2 gas is approximately the same as that of Al_2O_3 from O_2 (− 74·6 cal./degree/mole of sulphide).[28]

Barium

$$(2Ba + S_2 = 2BaS) \qquad \text{Accuracy } D$$
$$\Delta G^\circ_{298^\circ\text{K.}} = -222{,}000$$

The heat of formation of barium sulphide has been calculated by Bonhoeffer and Gruss[34] (p. 1517) from the measurement by Sabatier[54] of the heat of solution of BaS in HCl. This rather unreliable value has been used to calculate ΔG°, on the assumption that ΔS° is the same as for calcium sulphide. It is of interest to note that Sabatier's corresponding heat of solution of CaS in HCl,[54] and Bonhoeffer and Gruss's calculations,[34] lead to a heat of formation of 2CaS from S_2 of − 253·4 kg.cal., compared with von Wartenberg's now accepted value of − 259·6 kg.cal.

Calcium

$$(2Ca + S_2 = 2CaS) \qquad \text{Accuracy } A$$
$$\Delta G^\circ_{298\text{–}673^\circ\text{K.}} = -258{,}870 + 45{\cdot}62T$$
$$\Delta G^\circ_{673\text{–}1124^\circ\text{K.}} = -259{,}100 + 45{\cdot}92T$$
$$\Delta G^\circ_{1124\text{–}1760^\circ\text{K.}} = -263{,}560 + 49{\cdot}88T$$
$$\Delta G^\circ_{1760\text{–}2000^\circ\text{K.}} = -336{,}710 + 91{\cdot}44T \quad (\text{Accuracy } B)$$

Rosenqvist[52] has studied the equilibrium $CaS + H_2O = CaO + H_2S$ from 1023° to 1698° K. His results were combined with free-energy data for CaO, H_2O, and H_2S, and with the heat of transition, fusion, and evaporation of calcium from Kelley.[27, 25, 24]

The most recent and reliable value for the heat of formation of CaS is that obtained by von Wartenberg.[65] This gives − 259,620 cal. for $\Delta H^\circ_{298^\circ\text{K.}}(2CaS)$ from S_2 gas. If this result is coupled with the entropies of Ca, CaS, and S_2 obtained by Kelley,[27, 28] a value of − 245,520 cal. is obtained for $\Delta G^\circ_{298^\circ\text{K.}}$, compared with − 245,270 cal. calculated from the recommended equations. There is no measured heat capacity for CaS above 298° K.

The heat of formation of CaS calculated from Sabatier's measurement of the heat of solution of CaS in HCl is mentioned in the previous section on barium.

Cerium

$$(2Ce + S_2 = 2CeS) \qquad \text{Accuracy } C$$
$$\Delta G^\circ_{298\text{–}2200^\circ\text{K.}} = -267{,}000 + 40T$$

The cerium sulphides have been investigated by Brewer *et al.*[47] (p. 312), and their heats of formation have been calculated by Evans[47] (p. 312) from their heats of solution in HCl. The approximate free-energy equation given above is that proposed by Brewer on the assumption that $\Delta S \sim 20$ cal./degree. When combined with free-energy data on monatomic sulphur gas and cerium vapour, the equation agrees well with Brewer's measurements, between 2000° and 2400° K., of the vapour pressure of CeS, which vaporizes by decomposition to Ce and S gases. The approximate nature of the equation does not justify a change at the melting point of cerium, 1058° K.

Cobalt

$$(\tfrac{9}{4}Co + S_2 = \tfrac{1}{4}Co_9S_8) \qquad \text{Accuracy } A$$
$$\Delta G^\circ_{298\text{–}1048^\circ\text{K.}} = -79{,}240 + 39{\cdot}81T$$
$$(\tfrac{8}{3}Co + S_2 = \tfrac{2}{3}\text{`}\,Co_4S_3\,\text{'}) \qquad \text{Accuracy } A$$
$$\Delta G^\circ_{1048\text{–}1153^\circ\text{K.}} = -61{,}900 + 23{\cdot}21T$$

The equilibria between H_2S/H_2 mixtures and cobalt and its sulphides have recently been investigated by Rosenqvist.[53] He used a method in which errors due to thermal segregation in the gases were avoided. Rosenqvist has kindly given the authors permission to include his as yet unpublished data in this paper. The equations recommended for ΔG° have been derived from the following equations for the H_2/H_2S reactions.

$$\tfrac{9}{8}Co + H_2S = \tfrac{1}{8}Co_9S_8 + H_2$$
$$\Delta G^\circ_{873\text{–}1048^\circ\text{K.}} = -18{,}039 + 8{\cdot}10T \pm 200 \text{ cal.}$$
$$\tfrac{4}{3}Co + H_2S = \tfrac{1}{3}\text{`}\,Co_4S_3\,\text{'} + H_2$$
$$\Delta G^\circ_{1048\text{–}1153^\circ\text{K.}} = -9371 - 0{\cdot}16T \pm 150 \text{ cal.}$$

Rosenqvist reports that 'Co_4S_3' and CoS are not stoichiometric, and that the sulphide 'CoS' can exist in equilibrium with Co_9S_8 and 'Co_4S_3,' but not with metallic cobalt.

The measurements of Jellinek and Zakowski[18] of this equilibrium at 903° and 1003° K. (supposed by them

to be H_2/H_2S–Co/CoS) lead to ΔG° values about 2 kg.cal. more positive than those recommended here. This difference can, however, be attributed to the error arising from thermal segregation under the static gas conditions to which their results apply.

The heat of formation data of Thomsen[34] (*loc. cit.* p. 1529) and of Vanyukov and Kiseleva[61] have been disregarded, as they presumably apply to CoS.

Copper

($2'\ Cu_2S\ ' + S_2 = 4CuS$) Accuracy *B*

$\Delta G^\circ_{298\text{–}376^\circ K.} = -42{,}960 + 48{\cdot}46T$
$\Delta G^\circ_{376\text{–}623^\circ K.} = -44{,}800 + 53{\cdot}36T$
$\Delta G^\circ_{623\text{–}900^\circ K.} = -45{,}200 + 54{\cdot}00T$

Cuprous sulphide contains more sulphur than is represented by the formula Cu_2S when in equilibrium with CuS,[10] and its composition in this equilibrium varies with temperature. Its formula in the above equation is therefore written in inverted commas, and the ΔG° equations are calculated for the reaction of 1 mole of S_2 with cuprous sulphide to form CuS.

The equilibrium between copper sulphides and sulphur vapour has been studied by a number of investigators, whose results are reported by Kelley.[26] Those of Preuner and Brockmüller,[44] Allen and Lombard,[2] and Biltz and Juza[4] are in good agreement. Their data were combined with those of Preuner and Schupp,[45] so that the partial pressures of S_2 in the equilibrium gases could be calculated. These results lead to the equation recommended above for 623–900° K.

The lower temperature equations were calculated with the heats of transformation of stoichiometric Cu_2S given by Kelley.[27, 23] The transition assigned to 623° K. has not been confirmed by structural investigation, and is only a means of taking into account an abnormally high heat capacity at about this temperature.

The value of $\Delta G^\circ_{298^\circ K.}$, calculated from the above, is $-28{\cdot}5$ kg.cal. It compares reasonably with the value of $-25{\cdot}0$ kg.cal., which can be calculated from the heats of formation of CuS and stoichiometric Cu_2S, measured by von Wartenberg,[64] and the entropies at 298° K., recommended by Kelley.[28]

($4Cu + S_2 = 2Cu_2S$) Accuracy *B*

$\Delta G^\circ_{298\text{–}376^\circ K.} = -64{,}960 + 20{\cdot}17T$
$\Delta G^\circ_{376\text{–}623^\circ K.} = -63{,}120 + 15{\cdot}27T$
$\Delta G^\circ_{623\text{–}1356^\circ K.} = -62{,}720 + 14{\cdot}63T$

An equilibrium, presumably H_2/H_2S–Cu/Cu_2S, has been studied between 1000 and 1145° K. by Sudo[59] under flowing gas conditions, in which thermal segregation errors are probably avoided. His results were used for the equation proposed for temperatures above 830° K. A study of this same equilibrium by Cox *et al.*[12] (1000–1500° K.), who used a circulating gas stream, agrees fairly well with Sudo's results, although these workers probably had small thermal diffusion errors at the higher temperatures. Similar studies by Britzke and Kapustinskii[9] and Jellinek and Zakowski,[18] which give ΔG° values about 4 kg.cal. less negative, are subject to segregation errors and were disregarded. The equations below 623° K. were derived from the heats of transformation of Cu_2S given by Kelley[27, 23] (*see* remarks concerning these under CuS above).

Free-energy values may also be calculated from the heat of formation of Cu_2S from rhombic sulphur, measured by von Wartenberg (— 18,970 cal.)[64] and the necessary heat capacity and entropy data given by Kelley.[27, 28] These agree at 600° K., but are about 1·5 kg.cal. more negative at 1200° K.

Iridium

($\frac{4}{3}'\ Ir\ ' + S_2 = \frac{2}{3}'\ Ir_2S_3\ '$) Accuracy *B*

$\Delta G^\circ_{1000\text{–}1600^\circ K.} = -64{,}500 + 44{\cdot}66T$

This equilibrium has been measured by Biltz *et al.*[6] from 1293° to 1346° C. Their results lead to ΔG° values, which can be represented by the above equation. Since the measurements are few and there are no corroborating thermal data, a narrow temperature range is proposed.

The experimental results suggest that both Ir and Ir_2S_3 have some considerable solubility in each other, so that equilibrium does not occur between phases of constant composition. Both Ir and Ir_2S_3 are therefore written above in inverted commas. The ΔG° equation holds exactly for the reaction involving 1 mole of S_2.

Iron

($2'\ FeS\ ' + S_2 = 2'\ FeS_2\ '$(pyrite)) Accuracy *B*

$\Delta G^\circ_{600\text{–}1100^\circ K.} = -86{,}700 + 90{\cdot}07T$

Both ferrous and ferric sulphide are non-stoichiometric. When they are together in equilibrium with sulphur vapour, the ferrous phase contains more sulphur, and the ferric phase less sulphur than is represented by the formulae FeS and FeS_2,[19] the precise compositions depending on temperature. The ΔG° equations are calculated for the reaction of 1 mole of S_2 with pyrrhotite to form pyrite.

The equilibrium 'FeS_2'–'FeS'–S_2 has been studied between 840° and 960° K. by a number of investigators whose results are quoted by Kelley.[26] These are consistent and lead to the recommended equation.

An equation for the free energy of formation of FeS_2 of almost stoichiometric composition can be calculated from the following thermal data: heat of formation of pyrite — 42,500 cal. by Lipin, Uskov, and Klokman,[36] who used a combustion method; entropies at 298° K. from Kelley[28]; high-temperature heat capacities for Fe and S_2 from Kelley,[27] and for FeS_2 by Coughlin.[11] From these data, $\Delta H^\circ_{900^\circ K.} = -72{,}700$ cal. and $\Delta G^\circ_{900^\circ K.} = -30{,}400$ cal. (*see* Fig. 3). The free-energy equation for the stoichiometric reaction

$$2FeS + S_2 = 2FeS_2$$

(based on these data and the equation given below for FeS) is

$$\Delta G^\circ_{600\text{–}1200^\circ K.} = -73{,}600 + 68{\cdot}00T$$

This would lead to a value for $\Delta\mu_{S_2}$, in hypothetical equilibrium at 900° K. with the two stoichiometric phases, of — 12,400 cal., instead of the — 5700 cal. found for the equilibrium non-stoichiometric phases.

($2Fe + S_2 = 2FeS$) Accuracy *A*

$\Delta G^\circ_{298\text{–}412^\circ K.} = -74{,}320 + 31{\cdot}18T$
$\Delta G^\circ_{412\text{–}1179^\circ K.} = -71{,}820 + 25{\cdot}12T$
$\Delta G^\circ_{1179\text{–}1261^\circ K.} = -72{,}140 + 25{\cdot}48T$

These equations were derived from measurements made by Alcock and Richardson,[1] who studied the equilibrium between H_2/H_2S gas mixtures and iron and β-ferrous sulphide over the stoichiometric range.

In their experiments, the gases were circulated sufficiently fast to avoid errors in the H_2/H_2S ratios owing to thermal segregation of the gases. Their results agree closely with Sudo's measurements[57] of the same equilibrium, and also with similar measurements by Cox *et al.*[12,13] when allowance is made for the thermal segregation errors which must have been present at their slower rates of flow. Jellinek and Zakowski[18] and Britzke and Kapustinskii[8] studied the same equilibrium, but their results lead to free energies of formation which are considerably more positive than those recommended here. In the case of the former workers, the difference may be attributed, because of its size and sign, solely to the large thermal segregation error present under the static condition for which their results apply. The vastly different results of Britzke and Kapustinskii must be attributed to an unsatisfactory technique. The heats of transformation of FeS (α to β) and of Fe (α to γ) were taken from Kelley.[27] Free-energy values may also be calculated from the heat of formation of FeS measured by Zeumer and Roth[66] or by Kapustinskii and Korshunov,[21] and the thermal data given by Kelley[27, 28] and Coughlin,[11] the latter being for $FeS_{1.02}$. These agree at 298° K., but are about 0·9 kg.cal. more negative at 1200° K.

There is some indication that ferrous sulphide contains excess iron when in equilibrium with the metal at high temperatures.[11] This is contrary to the established phase diagram[3] and has not been taken into account.

Lead

$(2Pb + S_2 = 2PbS)$		Accuracy B
$\Delta G°_{298\text{-}600° K.}$	$= -72{,}710 + 34{\cdot}17T$	
$\Delta G°_{600\text{-}1387° K.}$	$= -75{,}160 + 38{\cdot}25T$	

Sudo[58] has studied the equilibrium H_2/H_2S–Pb/PbS from 855 to 1048° K. under conditions likely to be free from errors arising from thermal segregation in the gas mixture. His results were used for calculation of the equations, the heat of fusion of lead being taken from Kelley.[25]

The free-energy values may also be calculated from the heat of formation of PbS as measured by Zeumer and Roth[66] and other necessary thermal data given by Kelley.[27, 28] These agree reasonably, being about 2·3 kg.cal. more negative at 298° K. and 1 kg.cal. more positive at 900° K.

Jellinek and Zakowski[18] and Jellinek and Deubel[16] have also studied the H_2/H_2S ratios in equilibrium with Pb/PbS mixtures from 800 to 1273° K. Calculation from their results gives free energies of formation between 2 and 4 kg.cal. less negative than those obtained from Sudo's results, the differences being attributable to thermal segregation.

Magnesium

$(2Mg + S_2 = 2MgS)$		Accuracy C
$\Delta G°_{298\text{-}923° K.}$	$= -199{,}300 + 45{\cdot}6T$	
$\Delta G°_{923\text{-}1380° K.}$	$= -203{,}600 + 50{\cdot}3T$	
$\Delta G°_{1380\text{-}2000° K.}$	$= -268{,}700 + 97{\cdot}5T$	

The heat of formation of MgS from rhombic sulphur has been measured by Kapustinskii and Korshunov,[21] who used a bomb calorimeter and obtained a value of − 168,780 cal. for $\Delta H°_{298° K.}$. Solution calorimetry was used by von Wartenberg,[65] who obtained a value of − 167,800, and by Sabatier,[54] whose measurements lead to a value of about − 159,000 cal. The equations were calculated from the mean of the first two determinations and the assumption that $\Delta S°_{298° K.}$ for MgS is the same as for CaS. The heats of fusion and vaporization of Mg were taken from Kelley.[24, 25]

Manganese

$(2Mn + S_2 = 2MnS)$		Accuracy B
$\Delta G°_{298\text{-}1000° K.}$	$= -128{,}000 + 30{\cdot}64T$	
$\Delta G°_{1000\text{-}1374° K.}$	$= -129{,}070 + 31{\cdot}71T$	
$\Delta G°_{1374\text{-}1410° K.}$	$= -130{,}160 + 32{\cdot}50T$	
$\Delta G°_{1410\text{-}1517° K.}$	$= -131{,}020 + 33{\cdot}11T$	
$\Delta G°_{1517\text{-}1803° K.}$	$= -138{,}020 + 37{\cdot}72T$	
$\Delta G°_{1803\text{-}2000° K.}$	$= -125{,}540 + 30{\cdot}80T$	

The most recent and reliable published value for the heat of formation of manganese sulphide is that of Kapustinskii and Korshunov,[21] who used a bomb calorimeter to obtain a value of − 48,750 ± 520 cal. for $\Delta H°_{298° K.}$ per mole of MnS from rhombic sulphur. This has recently been confirmed by one of the present authors (J.H.E.J.), who has measured the heats of solution of MnS and MnO in HF. When combined with the heat of formation of MnO measured by Southard and Shomate[56] and the heats of formation of H_2O and H_2S, these results lead to − 49,190 ± 640 cal. for $\Delta H°_{298° K.}$

Since Kapustinskii and Korshunov's value was obtained in the more direct manner, it was combined with the appropriate entropy values from Kelley,[28] the high-temperature heat capacities of Mn and S_2 from Kelley,[27] and of MnS as measured by Coughlin.[11]

Jellinek and von Podjaski[17] have measured the equilibrium HCl/H_2S–MnS/$MnCl_2$, and Cox *et al.*[12] have measured the equilibrium H_2/H_2S–Mn/MnS. These results lead to free energies of formation of 2MnS of about 20 and 37 kg.cal. more positive than values given by the equations proposed in this paper. They are considered less reliable than the third-law values, and have been disregarded.

Molybdenum

$(Mo + S_2 = MoS_2)$		Accuracy C
$\Delta G°_{1073\text{-}1373° K.}$	$= -52{,}560 + 10{\cdot}2T$	

Parravano and Malquori[40] have measured the quantity of H_2S entrained in H_2 passed over a MoS_2–Mo mixture at temperatures between 805° and 1100° C. They have also shown that reduction almost certainly proceeds directly to Mo. By extrapolation, they have obtained the ratio H_2S/H_2 at zero flow rate and have taken this as the equilibrium ratio. Unfortunately, this is the condition for maximum thermal segregation. An approximate correction was made for the error caused by this effect on the basis of the measurements of Alcock and Richardson[1] in similar gas mixtures. The corrected results were then combined with the free-energy equation of H_2–H_2S. The small entropy term suggests, however, that the temperature dependence may be considerably in error, and the equation is therefore only recommended over a small range of temperature.

(MoS_3)

Parravano and Malquori[40] claim to have measured the equilibrium between sulphur vapour and the two molybdenum sulphides (MoS_3 and MoS_2) between

355° and 418° C. Their results suggest that MoS_3 is stable with respect to molten sulphur and MoS_2 at these temperatures, whereas the investigations of Biltz and Köcher[5] indicate the reverse. No equation for MoS_3 is therefore proposed.

Platinum

$$(2\text{'}\ PtS\ \text{'} + S_2 = 2PtS_2) \qquad \text{Accuracy } B$$
$$\Delta G^\circ_{700\text{–}1100^\circ\text{K.}} = -43{,}750 + 43{\cdot}8T$$

The equilibrium between the two platinum sulphides and sulphur vapour ($S_2 + S_6 + S_8$) has been measured by Biltz and Juza[4] from 889° to 964° K. The equilibrium S_2 pressures, which can be calculated with the data of Preuner and Schupp,[45] lead to the recommended equation. Since the measurements are few, a small temperature range only is proposed for the use of the equation.

The results of Biltz and Juza indicate that the lower sulphide in equilibrium with PtS_2 exists over a range of composition richer in sulphur than the formula PtS indicates. It is therefore written in the above equation within inverted commas, the equation holding precisely for the reaction involving 1 mole of S_2.

$$(2\text{'}\ Pt\ \text{'} + S_2 = 2\text{'}\ PtS\ \text{'}) \qquad \text{Accuracy } B$$
$$\Delta G^\circ_{1000\text{–}1700^\circ\text{K.}} = -66{,}100 + 43{\cdot}6T$$

This equilibrium has been measured by Biltz and Juza[4] from 1333° to 1459° K., under which conditions the sulphur is present almost entirely as S_2. Their results (but not their calculations) lead to ΔG° values which can be represented by the above equation. Since the measurements are few, and there are no corroborating data, a narrow range of temperature is proposed for its use.

The results of Biltz and Juza suggest that both PtS and Pt have some significant solubility in each other, so that the equilibrium does not occur between the pure stoichiometric substances. Both Pt and PtS are therefore written above in inverted commas. The ΔG° equation nevertheless holds precisely for the reaction involving 1 mole of S_2.

Silicon

$$(Si + S_2 = SiS_2) \qquad \text{Accuracy } D$$
$$\Delta G^\circ_{298^\circ\text{K.}} = -50{,}000$$

Sabatier[54] measured the heat of reaction for $SiS_2(c) + 2H_2O(l) = SiO_2 + 2H_2S$, and his result leads to a heat of formation of SiS_2 from crystalline silicon and sulphur gas of about 68 kg.cal. ΔG° was calculated on the assumption that ΔS° for SiS_2 is about the same as for SiO_2, − 44 cal./degree.[28]

Silver

$$(4Ag + S_2 = 2Ag_2S) \qquad \text{Accuracy } A$$
$$\Delta G^\circ_{298\text{–}452^\circ\text{K.}} = -44{,}800 + 22{\cdot}10T$$
$$\Delta G^\circ_{452\text{–}1115^\circ\text{K.}} = -41{,}980 + 16{\cdot}52T$$
$$\Delta G^\circ_{1115\text{–}1234^\circ\text{K.}} = -40{,}380 + 15{\cdot}09T$$
$$\Delta G^\circ_{1234\text{–}1500^\circ\text{K.}} = -51{,}800 + 24{\cdot}33T$$

Above 452° K. the equations are based on Rosenqvist's[51] measurements of the equilibrium H_2/H_2S–Ag/Ag_2S from 773° to 1073° K. They are considered the most accurate data available because a good circulating gas technique was used to prevent thermal segregation. The results of Watanabe,[62] Keyes and Felsing,[29] and Jellinek and Zakowski,[18] which lead to more positive values of ΔG°, can be attributed to thermal segregation. The more negative values, which can be calculated from the results of Pélabon[41] and Britzke and Kapustinskii,[9] have been disregarded. Other data used are the heat of fusion of Ag_2S, calculated from Rosenqvist's results, and the heat of fusion of Ag, from Kelley.[25]

The equation below 452° K. is based on the following: extrapolation of Rosenqvist's results to 452° K.; $\Delta H^\circ_{298^\circ\text{K.}}$ measured by Zeumer and Roth[66]; and $\Delta G^\circ_{298^\circ\text{K.}}$ derived from the e.m.f. measurements of Goates, Cole, Gray, and Faux[15] and of Kapustinskii and Makolkin.[22] The change of slope at 452° K. corresponds to a heat of transformation of Ag_2S from α to β, of 1410 cal., instead of the 1010 cal. recommended by Kelley.[27]

Sodium

$$(4Na + S_2 = 2Na_2S) \qquad \text{Accuracy } C$$
$$\Delta G^\circ_{298\text{–}371^\circ\text{K.}} = -208{,}000 + 56{\cdot}1T$$
$$\Delta G^\circ_{371\text{–}1187^\circ\text{K.}} = -210{,}500 + 62{\cdot}9T$$
$$\Delta G^\circ_{1187\text{–}1192^\circ\text{K.}} = -303{,}000 + 140{\cdot}8T$$
$$\Delta G^\circ_{1192\text{–}1600^\circ\text{K.}} = -300{,}600 + 138{\cdot}8T$$

The heat of formation of Na_2S used was that determined by Kraus and Ridderhof[33] by the addition of sulphur to sodium in liquid ammonia. The entropy of Na_2S at 298° K. was estimated as 23·6 cal./degree from the following values recommended by Kelley[28] for other substances: $CaSO_4 = 25{\cdot}6$; $CaS = 13{\cdot}5$; $Na_2SO_4 = 35{\cdot}7$. S°_{298} for sodium was taken from Kelley,[28] together with the values for the appropriate heats of fusion and vaporization.[24, 25]

Strontium

$$(2Sr + S_2 = 2SrS) \qquad \text{Accuracy } D$$
$$\Delta G^\circ_{298^\circ\text{K.}} = -237{,}000$$

The heat of formation of strontium sulphide has been calculated by Bonhoeffer and Gruss[34] (p. 1513) from the measurement by Sabatier[54] of the heat of solution of SrS in HCl. This rather unreliable value has been used to calculate ΔG°, on the assumption that ΔS° is the same as for calcium sulphide (*see also* under barium above).

Tungsten

$$(W + S_2 = WS_2) \qquad \text{Accuracy } C$$
$$\Delta G^\circ_{298\text{–}1400^\circ\text{K.}} = -62{,}360 + 23{\cdot}0T$$

Parravano and Malquori[40] have measured the quantity of H_2S entrained in H_2 passed over a WS_2–W mixture at temperatures from 795° to 1065° C. They have also shown that reduction proceeds directly from WS_2 to W. By extrapolation, they have obtained the ratio H_2S/H_2 at zero flow rate, and have taken this as the equilibrium ratio. Unfortunately, this is the condition for maximum thermal segregation. An approximate correction was made for the error caused by this effect on the basis of the measurements made by Alcock and Richardson[1] on segregation in similar mixtures. The corrected results were then combined with the free-energy equation for H_2–H_2S.

Zinc

$$(2Zn + S_2 = 2ZnS,\ \text{wurtzite}) \qquad \text{Accuracy } C$$
$$\Delta G^\circ_{298\text{–}693^\circ\text{K.}} = -121{,}130 + 45{\cdot}40T$$
$$\Delta G^\circ_{693\text{–}1180^\circ\text{K.}} = -123{,}480 + 48{\cdot}54T$$
$$\Delta G^\circ_{1180\text{–}1500^\circ\text{K.}} = -178{,}330 + 95{\cdot}00T$$

The most recent, and probably the most reliable, value for the heat of formation of ZnS is that determined by Kapustinskii and Korshunov[21] by direct measurement in a bomb calorimeter. They obtained the high-temperature form, wurtzite, presumably because of the rapid cooling of the calorimeter. The heat of formation of zinc blende was found to be 3·2 kg.cal. greater. This large difference seems improbable and, in addition, the temperature of transition is not known. Calculation was therefore made for wurtzite only.

The heat of formation was combined with the entropy and heat-capacity data from Kelley,[28, 27] the equation for gaseous zinc being obtained by extrapolation of that for liquid zinc and the latent heat of vaporization recommended by Kelley.[24] No allowance was made for the difference between the heat capacities of the blende and wurtzite forms.

Jellinek and Zakowski[18] have measured the H_2/H_2S ratio in equilibrium with Zn/ZnS, but their results are too erratic to be of any value.

References

1. C. B. Alcock and F. D. Richardson : *Nature*, 1951, vol. 168, pp. 661–662.
2. E. T. Allen and R. H. Lombard : *Amer. J. Sc.*, 1917, Series 4, vol. 43, pp. 175–195.
3. " Metals Handbook," Cleveland, Ohio, 1948 : American Society for Metals.
4. W. Biltz and R. Juza : *Zeitschrift für anorganische und allgemeine Chemie*, 1930, vol. 190, pp. 161–177.
5. W. Biltz and A. Köcher : *Ibid.*, 1941, vol. 248, pp. 172–174.
6. W. Biltz and others : *Ibid.*, 1937, vol. 233, pp. 257–281.
7. M. Bodenstein and W. Pohl : *Zeitschrift für Elektrochemie*, 1905, vol. 11, pp. 373–384.
8. E. V. Britzke and A. F. Kapustinskii : *Zeitschrift für anorganische und allgemeine Chemie*, 1930, vol. 194, pp. 323–350.
9. E. V. Britzke and A. F. Kapustinskii : *Ibid.*, 1932, vol. 205, pp. 95–112.
10. N. W. Buerger : *Economic Geology*, 1941, vol. 36, pp. 19–44.
11. J. P. Coughlin : *J. Amer. Chem. Soc.*, 1950, vol. 72, pp. 5445–5447.
12. E. M. Cox and others : *J. Met.*, 1949, vol. 185, pp. 27–31.
13. E. M. Cox and others : *Ibid.*, 1949, vol. 185, pp. 837–839.
14. A. G. Gaydon : " Dissociation Energies and Spectra of Diatomic Molecules," London, 1947 : Chapman and Hall.
15. J. R. Goates and others : *J. Amer. Chem. Soc.*, 1951, vol. 73, pp. 707–708.
16. K. Jellinek and A. Deubel : *Zeitschrift für Elektrochemie*, 1929, vol. 35, pp. 451–457.
17. K. Jellinek and G. von Podjaski : *Zeitschrift für anorganische und allgemeine Chemie*, 1928, vol. 171, pp. 261–270.
18. K. Jellinek and J. Zakowski : *Ibid.*, 1925, vol. 142, pp. 1–53.
19. R. Juza and W. Biltz : *Ibid.*, 1932, vol. 205, p. 278.
20. A. F. Kapustinskii and Yu. M. Golutvin : *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, 1951, No. 2, pp. 192–200.
21. A. F. Kapustinskii and I. A. Korshunov : *Acta Physicochimica SSSR*, 1939, vol. 10, pp. 259–272.
22. A. F. Kapustinskii and J. A. Makolkin : *Ibid.*, 1939, vol. 10, pp. 245–258.
23. K. K. Kelley : *Bull. U.S. Bur. Mines*, 1934, No. 371.
24. K. K. Kelley : *Ibid.*, 1935, No. 383.
25. K. K. Kelley : *Ibid.*, 1936, No. 393.
26. K. K. Kelley : *Ibid.*, 1937, No. 406.
27. K. K. Kelley : *Ibid.*, 1949, No. 476.
28. K. K. Kelley : *Ibid.*, 1950, No. 477.
29. F. G. Keyes and W. A. Felsing : *J. Amer. Chem. Soc.*, 1920, vol. 42, pp. 246–251.
30. J. A. Kitchener, J. O'M. Bockris and A. Liberman : *Disc. Faraday Soc.*, 1948, No. 4, pp. 49–60.
31. E. Klever : *Trans. Brit. Cer. Soc.*, 1929–30, vol. 29, Wedgewood Commemoration Section, pp. 149–161.
32. I. A. Korshunov : *Zhurnal fisicheskoĭ Khimiĭ*, 1939, vol. 13, pp. 703–704.
33. C. A. Kraus and J. A. Ridderhof : *J. Amer. Chem. Soc.*, 1934, vol. 56, pp. 79–86.
34. Landolt-Börnstein : " Physikalisch-Chemische Tabellen," Berlin, 1923, Hauptwerk II : Julius Springer.
35. G. N. Lewis and W. N. Lacey : *J. Amer. Chem. Soc.*, 1915, vol. 37, pp. 1976–1983.
36. S. V. Lipin, V. S. Uskov, and V. R. Klokman : *Zhurnal Prikladnoĭ Khimiĭ*, 1942, vol. 15, pp. 411–421.
37. J. C. Morris and R. C. Buehl : *J. Met.*, 1950, vol. 188, pp. 317–322.
38. " Selected Values of Chemical Thermodynamic Properties," Series III, 1947 onwards : National Bureau of Standards.
39. W. Nernst : *Zeitschrift für Elektrochemie*, 1903, vol. 9, pp. 622–627.
40. N. Parravano and G. Malquori : *Att. Rendiconti Accad. Lincei.*, 1928, Series 6, vol. 7, pp. 109–112, 189–192.
41. H. Pélabon : *Annales de chimie et de physique*, 1902, Series 7, vol. 25, pp. 365–432.
42. G. Porter : Discussions of the Faraday Society, 1950, No. 9, p. 65.
43. G. Preuner : *Zeitschrift für anorganische und allgemeine Chemie*, 1907, vol. 55, pp. 279–288.
44. G. Preuner and J. Brockmüller : *Zeitschrift für physikalische Chemie*, 1913, vol. 81, pp. 129–170.
45. G. Preuner and W. Schupp : *Ibid.*, 1910, vol. 68, pp. 129–156.
46. G. Preuner and W. Schupp : *Ibid.*, 1910, vol. 68, pp. 157–168.
47. L. L. Quill (Ed.) : " Chemistry and Metallurgy of Miscellaneous Materials—Thermodynamics," New York, 1950 : McGraw-Hill Book Co.
48. M. Randall and F. R. von Bichowsky : *J. Amer. Chem. Soc.*, 1918, vol. 40, pp. 368–375.
49. F. D. Richardson and J. H. E. Jeffes : *J. Iron Steel Inst.*, 1948, vol. 160, pp. 261–270.
50. F. D. Richardson, J. H. E. Jeffes, and G. Withers : *Ibid.*, 1950, vol. 166, pp. 213–235.
51. T. Rosenqvist : *J. Met.*, 1949, vol. 185, pp. 451–460.
52. T. Rosenqvist : *Ibid.*, 1951, vol. 3, pp. 535–540.
53. T. Rosenqvist : Private Communication.
54. P. Sabatier : *Annales de chimie*, 1881, Series 5, vol. 22, pp. 5–98.
55. C. W. Sherman, H. I. Elvander, and J. Chipman : *J. Met.*, 1950, vol. 188, pp. 334–340.
56. J. C. Southard and C. H. Shomate : *J. Amer. Chem. Soc.*, 1942, vol. 64, pp. 1770–1774.
57. K. Sudo : *Sc. Rep. Res. Inst.*, Tôhoku Univ., *A*, 1950, vol. 2, pp. 312–317.
58. K. Sudo : *Ibid.*, pp. 325–330.
59. K. Sudo : *Ibid.*, pp. 519–530.
60. G. B. Taylor and S. Lehner : *Zeitschrift für physikalische Chemie*, 1931, Bodenstein Festband, pp. 30–43.
61. V. A. Vanyukov and N. A. Kiseleva : *Jubeleinyi Sbornik Trudov Kafedry i Lab. Tyazhelykh Metallov Moskov Inst.*, 1939, No. 7, pp. 304–326.
62. M. Watanabe : *Sc. Rep. Res. Inst.*, Tôhoku Univ., 1933, vol. 22, pp. 902–914.
63. H. von Wartenberg : *Zeitschrift für anorganische Chemie*, 1908, vol. 56, pp. 320–326.
64. H. von Wartenberg : *Zeitschrift für physikalische Chemie*, 1909, vol. 67, pp. 446–453.
65. H. von Wartenberg : *Zeitschrift für anorganische und allgemeine Chemie*, 1943, vol. 252, pp. 136–143.
66. H. Zeumer and W. A. Roth : *Zeitschrift für physikalische Chemie A*, 1935, vol. 173, pp. 365–382.

Action of Inhibitors of Carbon Deposition in Iron Ore Reduction

By S. Klemantaski, Ph.D., D.I.C., A.R.C.S.

SYNOPSIS

It has been shown experimentally that at 450° C. reduction and carbon deposition during the reaction of carbon monoxide with Cumberland hematite ore can be controlled by the rate of gas flow and the addition of small concentrations of carbon-deposition inhibitors (cyanogen, ammonia, hydrogen, sulphide, carbon disulphide). On the basis of these and other experiments carbon deposition and its inhibition are considered. A method of determining the extent of carbon deposition in working blast-furnaces is suggested.

Introduction

Carbon deposition is the reaction :

$$2CO = C + CO_2, \quad \Delta H_0 = -41 \cdot 0 \text{ kg.cal.}$$

In practice the speed of this reaction becomes appreciable only when it is catalysed, and there has been considerable divergence of views on the nature of the catalysts. Much evidence, *e.g.*, the results of Baukloh and Henke,[1] now suggests that during the reduction of iron oxides metallic iron (or iron carbide) must be present for catalysis to take place.

At temperatures below about 560° C. the volumetric composition of the gas in equilibrium with Fe–Fe_3O_4 is about 50% CO_2 + 50% CO, whilst the gas in equilibrium with carbon is richer in CO_2. Carbon and iron oxide are, in fact, the products of ultimate equilibrium. It thus appears that carbon deposition is capable of seriously hampering the reduction of iron oxides, and such an effect has been observed by Bone, Reeve, and Saunders.[2]

Few determinations have been made of the extent to which carbon deposition occurs in blast-furnaces. From the gas-sampling data of Kinney, Royster, and Joseph[3] it appears that in their furnace 6–8% of the total carbon gasified was being deposited, a mean figure of about 9% being obtained from the data given by Saunders, Butler, and Tweedy[4] for a small experimental blast-furnace. Daws and Ridgion[5] concluded that carbon deposition in an actual furnace must have been well below 5%. Recently, Nowak[6] has given some curves of gas composition at various levels in a furnace working on fine ore, from which it is possible to estimate that about 13% of the total carbon gasified was being deposited.

Carbon deposition in the blast-furnace leads to the destruction of refractory materials and the swelling and disruption of the charge. It may also produce a carbon deposition–solution cycle, with important effects on the distribution of heat requirements with temperature (and hence on coke rate) : a hypothetical example is shown in Fig. 1. The possible existence of carbon deposition on a significant but unknown scale hinders the interpretation of operating data for the blast-furnace process ; the possible predominance of this reaction over reduction limits the conditions for direct processes. Thus, control of carbon deposition is desirable.

Various investigators have shown that carbon deposition can be controlled. For example, Diepschlag,[7] and Bone, Saunders, and Tress[8] have observed the stimulating effects of pressure and of hydrogen addition, respectively. Suppression of carbon deposition by preliminary treatment of the iron oxide has been reported, for example, by Baukloh and Helbrugge.[9] The same effect was obtained by Hibbott and Rees[10] and by Baukloh and Henke[1] by admixing cyanogen to the gas phase, the latter authors finding ammonia and hydrogen sulphide to behave similarly. Hartmann[11] quotes unpublished work showing that arsenic, too, is an inhibitor of carbon deposition.

The present investigation represents a first step in the detailed study of the action of carbon-deposition inhibitors in the reduction of iron ores.

PRELIMINARY EXPERIMENTS

Qualitative experiments at 450° C. confirmed Baukloh and Henke's report[1] of the striking inhibiting effects on carbon deposition over iron oxide of cyanogen, hydrogen sulphide, or ammonia, and showed carbon disulphide to have a similar effect. Cyanogen formation was detected when ammonia was being used as the inhibitor, suggesting intermediate nitride formation. The same results were obtained with iron powder (ex-carbonyl) in place of iron oxide. All samples produced hydrocarbons when dissolved in acid, indicating that the formation of iron carbide had not been stopped by the inhibitors.

MAIN EXPERIMENTS

Method

The method used to follow simultaneously the progress of reduction and carbon deposition was based on the determination of the change in weight of the iron oxide charge after a given time of reaction, and of the weight of CO_2 produced. The charge tends to gain weight as a result of the deposition on it of

Paper IM/B/18/51 (revised) of the Blast Furnace Process Committee of the Ironmaking Division of the British Iron and Steel Research Association, received 10th January, 1952.

Dr. Klemantaski is a member of the staff of the Ironmaking Division of the Association, working in the Blast Furnace Research Laboratory at Imperial College of Science and Technology, South Kensington.

carbon, and to lose weight through the removal of oxygen, as follows :

$$2CO = C + CO_2$$
$$FeO_m + nCO = FeO_{m-n} + nCO_2$$

It follows from stoichiometric considerations that if W_{CO_2} and ΔW are the weight of CO_2 and the change in weight of the charge, respectively, then the weights of CO used for reduction (R) and for deposition (D) are given by :

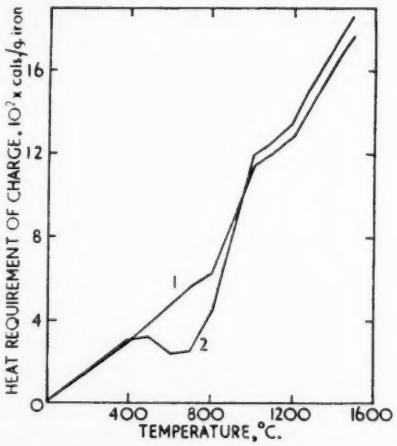
$$R = 0{\cdot}273\,W_{CO_2} - \Delta W$$
$$D = 0{\cdot}727\,W_{CO_2} + 2\Delta W$$

Apparatus and Procedure

The apparatus is shown in Fig. 2. A weight of $1{\cdot}000 \pm 0{\cdot}002$ g. of 10–16-mesh iron ore was weighed out on to a glass cloth mat in a Gooch crucible to form a single layer of pieces in loose contact. Tightly fitted into the adapter (7, Fig. 2), the crucible was then carefully inserted into the reaction tube (2). After stabilizing the temperature of the charge at $450° \pm 2°$ C. in a nitrogen atmosphere, the required flow of purified CO (mixed, when necessary, with a flow of inhibitor and/or hydrogen) was passed into the reaction tube through tap (3). The CO_2 and water in the exit gas were collected in a weighed absorbing train attached at tap (6). At the end of the run the reaction tube and train were flushed and filled with nitrogen, and the reaction tube was removed from the furnace and allowed to cool. The crucible (when cold) and the absorbing train were reweighed.

Temperatures were measured with the aid of the thermocouple in the sheath (4). The very slow flows of inhibitors were produced by displacement from an inclined gas burette by mercury flowing in under the action of water pressure. For both inhibitors and CO the control of flow rate was facilitated by the provision of blow-offs.

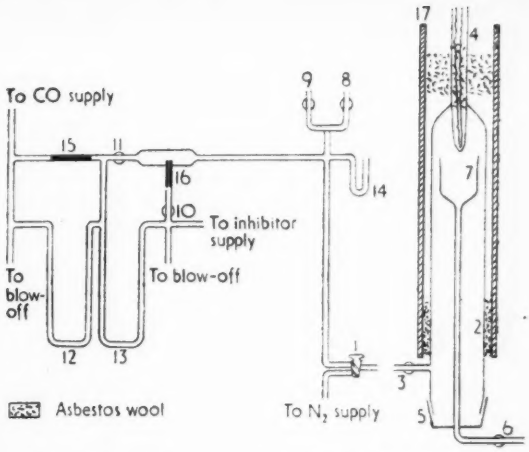
In most of the experiments Cumberland hematite ore was used, dried at 450° C. This is the ' ore *A* ' used



Line 1 : No carbon deposition ; carbon rate 11·8 cwt./ton pig
Line 2 : 2 cwt. of carbon deposited per ton of pig and consumed by reaction with CO_2 ; carbon rate 14·8 cwt./ton pig

Charge : Fe_2O_3, C, $CaCO_3$, and SiO_2 to give pig iron containing 4·0% C + 1·0% Si and slag of basicity 1·0 at the rate of 20 cwt./ton pig. Assumed 80% indirect reduction and no cooling losses or heats of formation or melting of slag

Fig. 1—Heat requirements up to 1500° C. of a hypothetical charge



1—Double-oblique tap
2—Reaction tube
3—Tap
4—Thermocouple sheath
5—Ground stopper
6—Tap
7—Adapter to hold Gooch crucible
8, 9, 10, 11—Taps
12, 13—Decalin-filled manometers
14—Mercury-filled manometer
15, 16—Capillary tubes
17—Tube of resistance furnace

Fig. 2—The apparatus

by the Bone–Saunders school, and has the following composition :

Fe_2O_3, %	SiO_2, %	Al_2O_3, %	CaO, %	H_2O (free), %	Mn, P, and S
82·36	14·63	0·23	0·90	0·6	Trace

Results

The weights of CO used for reduction and for carbon deposition were calculated from the equations given, with corrections (in the runs with hydrogen-containing gas) for loss in weight of the charge caused by hydrogen reduction. Mean values for the various conditions at 450° C. are shown in Table I. Figures 3 and 4 show the weights of CO used for reduction and for carbon deposition, respectively, plotted against time, and in Fig. 5 carbon deposition is plotted against reduction. The scales for degree of reduction in Figs. 3 and 5 are based on the CO equivalent of the total oxygen combined with iron in 1·000 g. of the ore, obtained from the mean of the analyses of three samples ; these scales are less accurate than the weight scales, and are not applicable to the runs with hydrogen-containing gas because of the appreciable reduction by hydrogen.

Figure 3 shows that the reduction process tends to reach a limit, which can be increased by increasing the rate of flow of CO or by using inhibitors of carbon deposition. The limit varies from about 45% reduction with pure gas, flowing at 0·35 ml./sec.,* to over 95% with the same flow, accompanied by 0·75 vol.%† of cyanogen, or a flow of 2·75 ml./sec. containing 0·1 vol.% of cyanogen. Other conditions, *e.g.*, 1 ml./sec. of CO together with $2{\cdot}75 \times 10^{-3}$ ml./sec. of cyanogen, also seem to lead to almost complete reduction. The effect of hydrogen is to lower both the weight of CO taking part in reduction and also the degree of reduction ; it also evidently lowers the effect on the reduction process of an admixture of

* ' ml.' is used for ' standard millilitre.'

† ' vol.% ' indicates ' volumes per 100 volumes of CO.'

Table I

RESULTS OF EXPERIMENTS WITH CO AT 450° C. AND 10–16-MESH CUMBERLAND HEMATITE, WITH AND WITHOUT CARBON-DEPOSITION INHIBITORS

Ref. No. in Figs. 3, 4, and 5	Rate of Flow of CO, ml./sec.	Rate of Flow of Inhibitor, ml./sec. $\times 10^{-3}$	Conc. of Inhibitor, vols./100 vols. CO	Duration of Run, min.	Mean Wt. of CO Used for Reduction, g.	Mean Wt. of CO Used for Carbon Deposition, g.	No. of Runs on which Means are Based	Variance of Results of Runs $\times 10^4$		Max. Calculated CO_2 in Exit Gas, vol. %
								Reduction	Deposition	
	Inhibitor: None									
1	0·35	...	...	30	0·113	0·076	5	0·05	0·14	39
	,,	...	...	60	0·162	0·348	5	0·22	17·55	
	,,	...	...	90	0·186	0·785	2	0·30	0·01	
	,,	...	...	120	0·194	1·14	3	0·26	18·80	
2	0·50	...	...	30	0·137	0·118	2	0·01	0·01	
3	1·0	...	...	30	0·180	0·268	3	1·00	2·73	25
	,,	...	...	60	0·265	0·801	1	...	...	
	,,	...	...	90	0·302	1·60	2	1·44	200·0	
	,,	...	...	120	0·305	2·48	3	2·53	1640·0	
4	1·55	...	...	30	0·205	0·355	2	<0·01	<0·01	
5	2·75	...	...	30	0·243	0·500	5	0·15	7·15	11
	,,	...	...	60	0·344	1·62	2	0·09	2·75	
	,,	...	...	90	0·390	2·67	2	3·64	2·00	
6	5·50	...	...	30	0·265	0·755	3	0·05	102·6	
	Inhibitor: Cyanogen									
7	0·35	0·525	0·150	30	0·141	0·052	3	0·05	0·17	40
	,,	,,	,,	60	0·233	0·216	3	0·09	2·75	
	,,	,,	,,	120	0·252	1·08	2	2·42	72·0	
8	0·35	1·05	0·300	30	0·148	0·061	2	0·32	0·02	24
	,,	,,	,,	60	0·265	0·183	2	0·72	3·12	
	,,	,,	,,	120	0·359	0·619	2	0·84	15·68	
9	0·35	2·62	0·750	30	0·167	0·078	2	0·24	0·05	30
	,,	,,	,,	60	0·310	0·219	3	0·39	6·42	
	,,	,,	,,	120	0·422	0·368	2	0·98	7·22	
10	1·0	1·00	0·100	60	0·325	0·543	2	0·02	1·80	
11	1·0	2·75	0·275	30	0·258	0·144	2	0·12	2·00	8
	,,	,,	,,	60	0·379	0·267	2	<0·01	0·50	
12	2·75	2·75	0·100	9	0·132	0·051	2	0·72	0·32	6
	,,	,,	,,	15	0·194	0·096	1	...	...	
	,,	,,	,,	30	0·311	0·226	2	0·13	0·02	
	,,	,,	,,	45	0·351	0·321	2	0·61	2·00	
	,,	,,	,,	90	0·425	0·723	2	0·50	0·04	
13	2·75	5·50	0·200	30	0·324	0·199	2	0·40	0·18	
14	2·75	13·9	0·504	30	0·275	0·177	1	...	...	
15	5·50	2·75	0·050	30	0·305	0·254	2	0·12	0·72	
	Inhibitor: Ammonia									
16	2·75	1·30	0·047	30	0·307	0·214	2	<0·01	0·08	
17	2·75	2·30	0·084	30	0·340	0·246	2	<0·01	0·72	
18	2·75	7·00	0·254	30	0·322	0·209	2	0·12	0·18	
	Inhibitor: None									
19	0·35	...	...	60	0·126	0·744	3	4·42	29·06	*
	Inhibitor: Cyanogen									
20	0·35	2·62	0·750	60	0·179	0·664	3	1·53	21·07	†

* 5 vols. H_2/100 vols. of CO: reduction of ore 34%.
† 5 vols. H_2/100 vols. of CO: reduction of ore 47%.

0·75 vol.% of cyanogen. The few runs with ammonia as the inhibitor showed that its effect on reduction and carbon deposition was similar to that of cyanogen. For both inhibitors there appears to be an optimum concentration giving maximum rates of reduction in the first 30 min.

There is a tendency (Fig. 4) for the rate of carbon deposition to become steady with increasing time. With pure CO these steady rates do not increase linearly with the rate of gas flow but become less susceptible to changes with increasing flow rate (Fig. 6). Thus at the higher rate of flow carbon deposition is not limited by the rate of supply of gas.

With a flow of CO of 2·75 ml./sec. (Fig. 4) the presence of cyanogen in a concentration of 0·1 vol.% decreases the extent of carbon deposition in 60–90 min. by about 70%. The efficacy of a given concentration of the inhibitor apparently increases with higher rates of flow of CO. This may be seen by comparing the weights of CO used for carbon deposition in 60 min. for the gas containing 0·1% of cyanogen and flow rates of 1·0 and 2·75 ml./sec. with the corresponding weights for the pure gas.

Considering again the weights of CO used for carbon deposition in 60 min., the addition of hydrogen produced a relative increase of approximately 114%. The effect of 0·75 vol.% of cyanogen on the hydrogen-stimulated carbon deposition was a relative decrease of approximately 11%, which may be compared with the corresponding figure of 37% for runs without hydrogen ; but there is much less difference between the absolute effects of this concentration of cyanogen in the two cases.

The method of plotting used in Fig. 5 brings out more clearly the nature of the reduction limits, as the degree of reduction above which the carbon-deposition reaction absorbs virtually the whole of the total CO reacting. For instance, with pure CO flowing at 1 ml./sec. it is evidently almost impossible to obtain a degree of reduction greater than about 74% (line 3 becomes almost vertical). On the other hand, by adding 0·1 vol.% of cyanogen, reduction over 74% can be obtained with a moderate consumption of CO by carbon deposition (point 10, Fig. 5).

Some or all of the carbon deposited on the ore is available for the completion of reduction by the process represented by :

$$FeO_n + nC \rightarrow Fe + nCO$$

The broken line in Fig. 5 shows the relationship between the extents of reduction and carbon deposition by CO to give a product containing the quantity of carbon required for the foregoing process. The field above this line represents carbon deposition which, from this point of view, is excessive, and, conversely, below the line carbon deposition is insufficient.

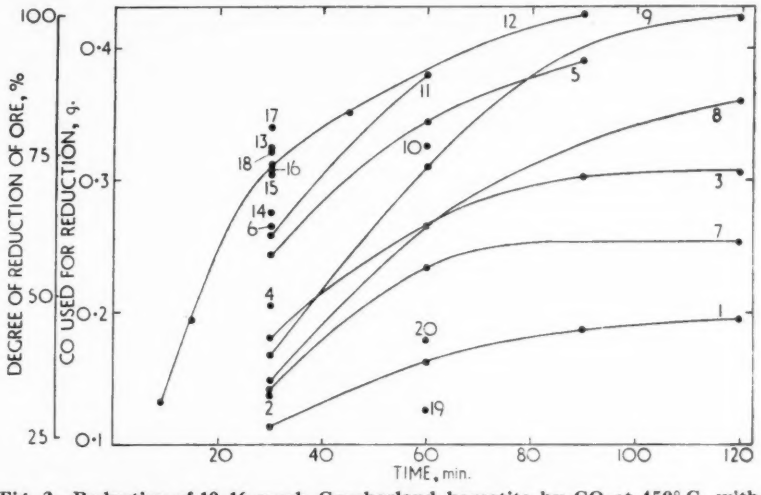


Fig. 3—Reduction of 10–16-mesh Cumberland hematite by CO at 450° C. with various flow rates and concentrations of admixed gases (for key to curves *see* Table I)

Within the range of gas flows and compositions used, the degrees of reduction conforming to the relationship represented by the broken line could be varied from about 30–40% to about 75%.

ADDITIONAL EXPERIMENTS

Some additional experiments, the results of which are of interest in a general discussion of the main experimental results, are briefly described below.

Effect of Temperature on Distribution of CO between Reduction and Carbon Deposition

The apparatus and procedure were as for the main experiments, but runs were carried out at temperatures of 480°, 460°, 440°, and 420° C. All runs were for 90 min. with pure CO flowing at 1 ml./sec., and Cumberland hematite was used throughout. The results are plotted in Fig. 7.

The ratio of the extent of carbon deposition to that of reduction increases with temperature throughout the range, the value at 450° C. being clearly well below the maximum. In this range the reduction reaction apparently has a negative temperature coefficient.

Effect of Reaction with CO on Temperature of Iron Oxide Charge

Because carbon deposition is strongly exothermic, differences must be expected between the 'temperature of the experiment,' as measured by the reaction-tube thermocouple, and the temperature of the solid charge. This was qualitatively confirmed by making a run with the apparatus slightly modified to permit a thermocouple to be in contact with the charge in the crucible. Powdered Ouenza ore and pure CO flowing at 7 ml./sec. were used ; whereas the temperature of the experiment remained at 450° ± 2° C., that of the thermocouple in contact with the ore rose to 488° C. within 1 min. after the start of the run (probably through the rapid and exothermic first stage of the reduction of ferric oxide) ; it then dropped to 455° C. and thereafter rose more or less steadily to 492° C. at the end of 15 min., when the experiment was stopped.

Effect of Cyanogen on Reaction of CO_2 with Iron

That the oxidation of iron by CO_2 is hindered by cyanogen at 450° C. was shown in the following manner. Over a 2·00-g. charge of iron powder (ex-carbonyl) at 450° C. a fixed volume of CO_2 or of CO_2 containing 1·0 vol.% of cyanogen was passed at 1 ml./sec. under standard conditions, a fresh charge of iron being used for each run. The volume of CO produced in each run (which is a measure of the extent of the reaction) was determined from the volume and CO content of the exit gas, collected over caustic potash solution. The volumes (N.T.P.) of CO produced in the runs with pure CO_2 were 59, 58, and 58 ml., and those in runs with the cyanogen-containing gas were 43 and 42 ml. The means of these two sets of figures are significantly different.

Action of CO on Natural Magnetites

Using the apparatus and procedure of the main experiments, no appreciable reduction or carbon deposition took place at 450° C. with 10–16-mesh Kiruna or Grangesberg ore treated with pure CO for 30 min.

GENERAL DISCUSSION

Very small concentrations of cyanogen or ammonia have radical effects on carbon deposition and ore reduction. This suggests that results of interest in

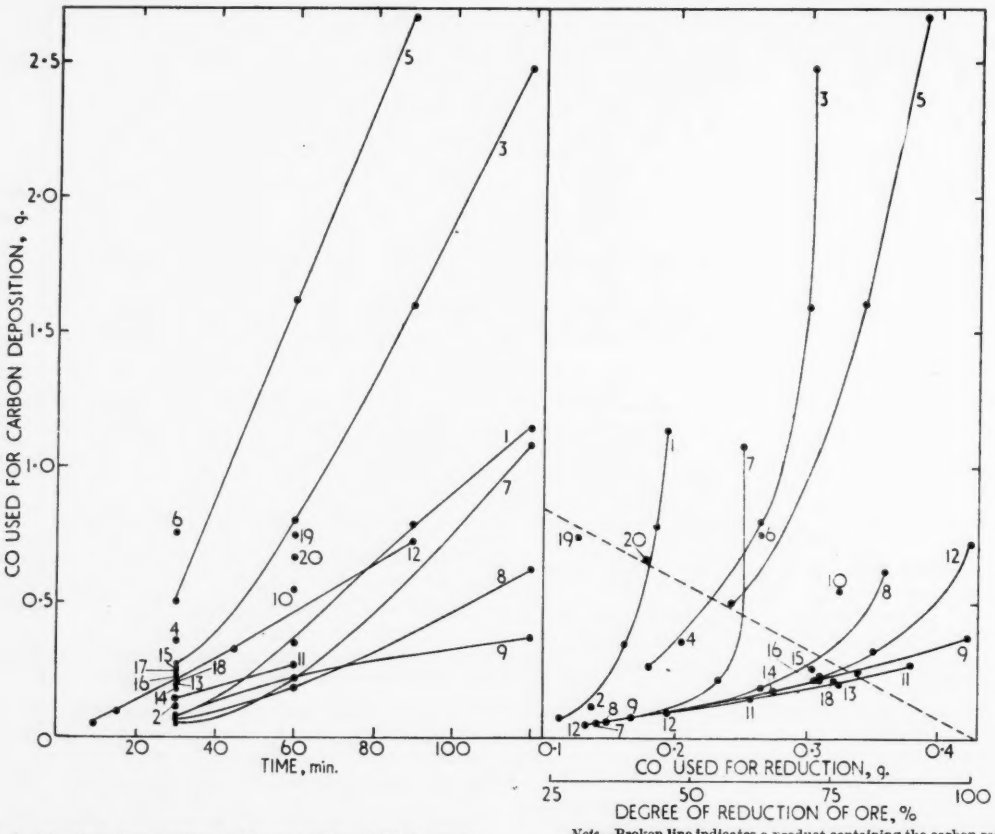


Fig. 4—Carbon deposition in the reaction of 10–16-mesh Cumberland hematite with CO at 450° C. with various flow rates and concentrations of admixed gases (for key to curves *see* Table I)

Note—Broken line indicates a product containing the carbon required to complete the reduction of iron oxide giving CO

Fig. 5—Carbon deposition and ore reduction in the reaction of 10–16-mesh Cumberland hematite with CO at 450° C. with various flow rates and concentrations of admixed gases (for key to curves *see* Table I)

the blast-furnace process may follow from a systematic study, using sensitive methods, of the occurrence of the minor components of the gas in the blast-furnace.

Being heterogeneous, carbon deposition may be considered to involve, very broadly, three processes in addition to the formation of the catalyst (if not already present): (i) Adsorption on the catalyst, (ii) reaction on the catalyst, and (iii) regeneration of the surface of the catalyst by the decomposition or removal of reaction products. Inhibition may thus be due to interference with one or more of these processes. Although the experimental conditions in the present investigation were not suitable for the detailed study of reaction mechanism, some tentative conclusions may be drawn.

The results suggest that the iron oxides and the deposited carbon had negligible catalytic effects on carbon deposition. Thus magnetites were not reduced and did not catalyse carbon deposition; carbon deposition was rapid at very high degrees of reduction of Cumberland hematite, when the concentration of iron oxide was very small, and also with iron powder; the rates of carbon deposition tended to constant values, which were not caused by limitations in the gas supply, whereas if the deposited carbon were itself a catalyst the rates would have increased rapidly to the greatest value permitted by the rate of supply of gas.

From the results it seems unlikely that the action of the carbon-deposition inhibitors is due to interference with the formation of the catalyst or with the regeneration of the catalyst surface by removal of CO_2. There are indications (for example, the work of Jack[12] on the reaction of CO with iron nitride) that inhibition is caused by the formation of compounds interfering with the movement of carbon atoms over and into the catalyst.

The study of the action of the carbon-deposition inhibitors on the basis of the results reported is greatly complicated by the fact that (*a*) the temperature of the catalyst differs by large and unknown amounts from the temperature of the experiment, and (*b*) the rate of carbon deposition increases on raising the temperature above 450° C. These two effects imply that the action of the inhibitors may be due not only to the causes considered above, but also to their action in minimizing the rise in temperature of the catalyst. The opposite considerations, however, apply to the stimulating effect of hydrogen. On the other hand, in 'inhibited' runs, the concentrations of CO and of the catalyst (iron or iron carbide) tend to be greater than in similar runs with the pure gas, so that the observed action of the inhibitors has been relatively minimized.

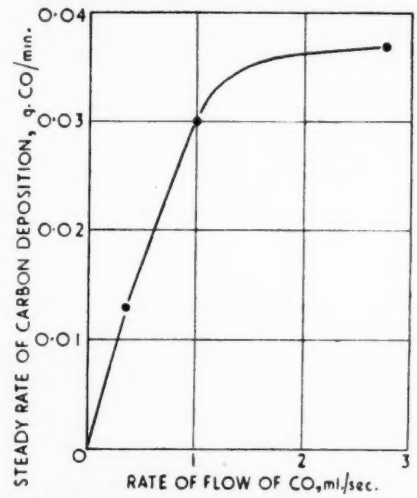


Fig. 6—Steady rate of carbon deposition at various rates of gas flow during the reaction of 10–16-mesh Cumberland hematite with CO at 450° C.

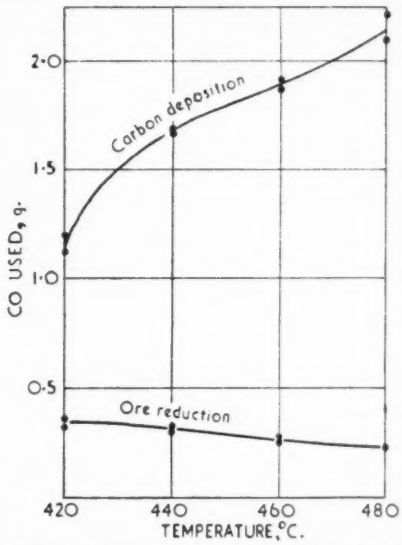


Fig. 7—Effect of temperature on the reaction of CO, flowing at 1 ml./sec., with 10–16-mesh Cumberland hematite. Reaction time: 90 min.

To explain the stimulating effects of the carbon-deposition inhibitors on reduction, the ways in which this reaction is normally interfered with by carbon deposition must be considered. As soon as the outside of an ore particle has been fully reduced, the reduced layer becomes the seat of the carbon-deposition reaction. This reduces the amount of CO available for reduction, decreases its reducing propensities by contamination with CO_2, reduces the gas concentration gradients from the inside (where reduction is going on) to the outside, and tends to block the pores with deposited graphite. In an isolated particle the last effect is to some extent counteracted by the disruption of the ore caused by the crystallization of the graphite, but in a bed this disruption leads to the choking of the voids and to channeling. The favourable action of the inhibitors on reduction is thus readily understandable.

The same size range of ore particles was used in all the experiments of the present investigation. Figure 5 indicates that the inhibitors become appreciably active only at relatively high degrees of reduction, suggesting, perhaps, that with larger particles a great deal of carbon deposition might occur before it is suppressed. However, with a large particle

it will not be the degree of reduction of the whole that will be important, but only that of the catalytically active (outer) layer. There would thus seem to be no reason to expect a failure of inhibition with larger particles ; but the rate of consumption of the inhibitor in the outer layers may prevent it from penetrating to the deeper layers.

It has been shown that the efficacy of a given concentration of inhibitor increases with increasing rate of flow of gas, possibly because the rate of production of new reduced surface will tend to a limit, further increases in flow rate thus leading to a relative increase in the rate of arrival of the inhibitor at the active surface. The same effect may be expected with N_2–CO–CO_2–H_2 mixtures, but here the possible effect of hydrogen in clearing the catalyst of the inhibiting groups is a possible complication. Further experimental study is necessary before extrapolations can be made to wider conditions of gas flow.

Hibbott and Rees[10] obtained their inhibiting effect with initial cyanogen concentrations of over 1·5%, but at lower concentrations cyanogen appeared actually to stimulate the reaction. A possible explanation of this discrepancy is as follows. The experiments were carried out with samples of firebrick and with relatively small, and not replenished, quantities of cyanogen. The cyanogen first inhibited carbon deposition in the normal way, consequently stimulating the reduction of the iron spots, but was then removed from the system by combination (sublimates were, in fact, observed). The result was a firebrick with more active spots of reduced iron than after treatment with pure CO. With the higher initial concentrations of cyanogen the amount of gas involved was evidently sufficient to maintain inhibition throughout an experiment.

It should be possible to determine the normal rate of carbon deposition in a blast-furnace by noting the change in top-gas composition corresponding to a change, to a known relative extent, in the rate of the reaction, the change being made in such a way that the rates of the various carbon gasification reactions are unaffected. From the results of this investigation it appears that inhibition of carbon deposition may be a practicable method of effecting the required change without interfering with the operation of the furnace ; further work would be necessary to confirm this.

SUMMARY OF RESULTS AND CONCLUSIONS

Interaction of CO at 450° C. and a Single Layer Charge of Cumberland Hematite

(1) Cyanogen, ammonia, hydrogen sulphide, and carbon disulphide have been confirmed as inhibitors of carbon deposition, cyanogen and ammonia being effective in concentrations of 0·05 vol.%

(2) The rate of reduction is increased by the addition of cyanogen or ammonia or by increase in the rate of flow of CO.

(3) The presence of 5 vol.% of hydrogen in the CO stimulates carbon deposition but hinders reduction and impairs the inhibiting action of cyanogen.

(4) By a suitable choice of flow rates and gas composition, the composition of the products of the reaction can be controlled over a wide range.

(5) The catalytic effect of iron oxide and deposited carbon on carbon deposition is negligible.

Other Conclusions

(1) In the range of temperature of CO of 420–480° C., the rate of reduction of Cumberland hematite decreases and that of carbon deposition increases with increasing temperature.

(2) Cyanogen decreases the reaction of CO_2 with iron at 450° C.

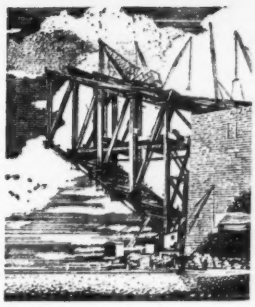
(3) The inhibitors of carbon deposition are effective with iron powder.

(4) The effects of CO at 450° C. on Kiruna or Grangesberg ore (10–16 mesh) are negligible.

(5) After further study it may be possible to use the carbon-deposition inhibitors for determining the extent of this reaction in blast-furnaces and for developing new reduction methods.

References

1. W. Baukloh and G. Henke : *Metallwirtschaft*, 1940, vol. 19, p. 463.
2. W. A. Bone, L. Reeve, and H. L. Saunders : *J. Iron Steel Inst.*, 1927, No. I, p. 127.
3. S. P. Kinney, P. H. Royster, and T. L. Joseph : *U.S. Bur. Mines*, 1927, *Tech. Paper* 391.
4. H. L. Saunders, G. B. Butler, and J. M. Tweedy : *J. Iron Steel Inst.*, 1949, vol. 163, p. 173.
5. L. F. Daws and J. M. Ridgion : B.I.S.R.A. Restricted Report IM/B/21/49.
6. E. Nowak : *Stahl u. Eisen*, 1950, vol. 70, p. 829.
7. E. Diepschlag : *Arch. Eisenhüttenwesen*, 1937, vol. 9, p. 179.
8. W. A. Bone, H. L. Saunders, and H. J. Tress : *J. Iron Steel Inst.*, 1938, No. I, p. 85P.
9. W. Baukloh and J. Helbrugge : *Arch. Eisenhüttenwesen*, 1941, vol. 15, p. 163.
10. H. W. Hibbott and W. J. Rees : *Trans. Cer. Soc.*, 1933, vol. 32, p. 253.
11. F. Hartmann : *Stahl u. Eisen*, 1940, vol. 60, p. 1021.
12. K. H. Jack : *Proc. Roy. Soc.*, 1948, *A*, vol. 195, p. 41.



THE IRON AND STEEL ENGINEERS GROUP

REPORT OF THE SIXTEENTH MEETING

The Sixteenth Meeting of The Iron and Steel Engineers Group of The Iron and Steel Institute was held at 4 Grosvenor Gardens, London, S.W.1, on Tuesday, 4th December, 1951. Mr. C. H. T. Williams (The Park Gate Iron and Steel Co., Ltd.), Chairman of the Group, was in the Chair.

The Morning Session was occupied by the presentation and discussion of the paper, "Cooling Beds for Bar Mills," by W. Udall (Brightside Foundry and Engineering Co., Ltd.).

The Afternoon Session was devoted to the reading and discussion of a paper by G. Foster (Dorman Long and Co., Ltd.) entitled, "Some Comparisons between British and American Rolling Mill Practice," copies of which were available for those attending the meeting; the discussion on this paper was published in the May issue of the *Journal*.

PROCEEDINGS OF THE MORNING SESSION: 10.30 A.M. to 12.45 P.M.

Discussion on the Paper—

COOLING BEDS FOR BAR MILLS*

Mr. **W. Udall** (The Brightside Foundry and Engineering Co., Ltd.), in introducing his paper, gave further information on the cooling of bar steel that had come to hand since going to press. Figure *A* shows the theoretical computations and experimental results for cooling bar sizes from $\frac{7}{8}$ in.–1$\frac{3}{4}$ in. to temperatures at which they could be handled safely. In the absence of instruments the surface temperature was assumed to be about 180° F. when the bar could be touched with the hand for a few seconds without acute discomfort. The calculations were based on the same assumptions as those used for Figs. 14, 16, and 17; the practical results fell within the extremes of 170° and 190° F.

Mr. Udall pointed out that Figs. 8*b* and *c* were transposed in the paper as printed.

Mr. **T. W. Hood** (Samuel Fox and Co., Ltd.): In a single-sided mechanical cooling bed preceded by a flying shear the finishing stand of the mill is usually a long way from the beginning of the bed. Could this distance be lessened to reduce the length and the cost of the mill building? The beds described by Mr. Udall need time for the throw-off mechanism to operate, obtained by having a distance between flying shear and bed sufficient to accelerate the front bar until it has the required lead on the one following.

Two other designs of bed, both of European manufacture, which avoid this long run-in, make the throw-off device cover only that half of the width of the hot run-in rollers nearest the bed, and direct the front end of each bar slightly away from the bed so that it runs clear of the throw-off for some distance. The flying shear can then be much nearer to the bed. One of these designs lifts the bar off the run-in rollers by means of shovels attached to the moving notched bars; the other uses triangular plates which, when raised, throw the bar into the first notch. Both appear to operate satisfactorily.

Part of the distance I have mentioned is in some designs due to the throw-off and first notch beginning before the bed itself to allow the bar to come to rest with almost the full length of the bed available for cooling. This feature would be less simple to incorporate on the first type of bed mentioned.

In regard to the straightness of bars, one roller-type bed gave a pronounced kink near the centre of fairly small bars, probably owing to the sticking of some of the pawls operating the rollers, so that the portion of the bars on them tended to lag behind. The notched bed holds the bars more positively.

Notched bars vary from heavy machined cast-iron to mild-steel flats profiled to the notch shape, and as little as $\frac{3}{8}$ in. thick. These are reasonably free from warping, and although they probably wear quickly, they could be readily replaced and would appreciably reduce the initial cost of the bed. Symmetrical notches are probably best

* *J. Iron Steel Inst.*, 1951, vol. 169, pp. 257–276.

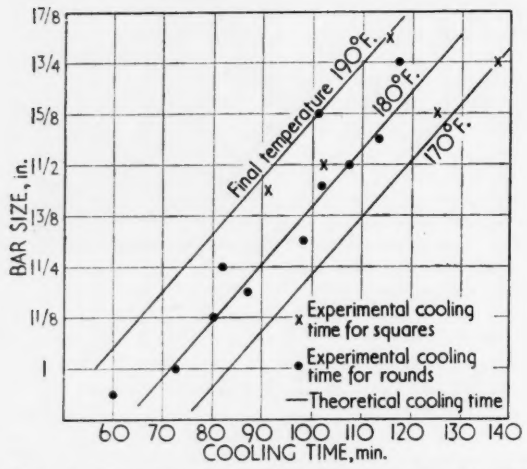


Fig. A—Experimental cooling times compared with theoretical cooling times

for rounds only, but unsymmetrical notches are better when flats are also rolled, as in most mills; both types are in use.

Straightening by impact is variously provided, the Edwards bed being probably the best, as it provides impact at every notch. In modern beds the number of impact notches is either two, one, or none. What governs the number of impact notches required?

A common method of straightening spring flats in hand mills is to stack them between rows of posts in cooling stands. This prevents sweep and gives some degree of pack annealing. Is there no tendency to sweep when the flats are packed on edge on a mechanical bed, caused by unequal cooling of the top and bottom edges?

Can the author tell us how the temperatures in the cooling curves were taken, and in particular whether the bar was standing in one notch or travelling across the bed in normal production?

The examples in Figs. 15*c* and *d* of bars of about the same *W*/*A* ratio (*i.e.*, those of $\frac{3}{4}$-in. dia. or equivalent) appear to indicate that the cooling rate is increased by the roller bed. Thus the 18-mm. round in Fig. 15*d* cools from 1600–400° F. in three-quarters of the time that would be expected from the theoretical curves, and similarly with the 16-mm. round in Fig. 15*c*.

Figure 15*e* suggests that a $\frac{3}{4}$-in. round cools in much the same time when pack-annealed as would be expected from theory without pack annealing; the same appears to hold in Fig. 15*f* for $\frac{7}{8}$ in. × $\frac{5}{8}$ in. and $\frac{3}{4}$ in. × $\frac{1}{2}$ in. bars.

The figures for the tonnage cooled given in Fig. 18 for a range of bar diameters appear rather high, and this is borne out by comparison with a theoretical capacity based on Fig. 17 and with Fig. 4 of Raisig's paper.* The cooling capacity for a $\frac{3}{4}$-in. dia. bar from Fig. 18 is 450 lb./hr./ft. length cooled. Assuming the cooling range to be 1600–450° F., Fig. 17 gives the cooling time as 15 min., so that a bed with 20 notches would cool 120 lb./hr./ft. length. Doubling this to allow for cooling on the shuffle bars brings it to 240 lb./hr./ft. length cooled. The corresponding capacity from Raisig's paper is 250. Does Fig. 18 perhaps represent a double-sided bed?

Mr. **W. Udall**: The location of the cooling bed in relation to the flying shear, and its effect on the cost of the buildings housing it, is an important factor in plant layout. Any attempt to condense a high-output rolling-mill plant into the minimum space is short-sighted, inevitably causing congestion and precluding the operation of the mill beyond its nominal designed capacity even for relatively short periods. The main factor governing the relative location of the cooling bed and the shear is usually the need for a gap between successive cut lengths to allow the bar throw-off mechanisms to function. The more popular forms of these are shown in Figs. 3 and 7, and are located above the run-in table. They are designed to sweep forward to transfer the bar to the straightening pocket and return to an ambushed position. Until the throw-off mechanism has returned to this position the following bar cannot enter the throw-off section of the run-in table. An exception to this form of throw-off gear is shown in Fig. 8*b*.

It would appear from Mr. Hood's description of the two European beds that, because the two bars are conveyed at different speeds on the run-in table, at least one is subjected to rubbing contact with the table rollers. Whilst this may be acceptable for some forms of section and qualities of steel, it may be undesirable when the quality of surface finish is important.

The throw-off mechanism described by Mr. Hood is similar to that shown on the disc-roller tables in Fig. 5, which is the type of cooling bed employed on the semi-continuous mill illustrated in Fig. 1*c*. In this layout the cooling bed is a long way from the three flying shears. This distance was probably determined by the need to accelerate the cut lengths delivered to the horizontal roller table, which used hinged plates (Noll plates) for discharging the bar from the table. If disc-type roller tables only had been used on this cooling bed the distance between the bed and the shears could have been reduced.

Whatever form of bed mechanism is used, operating economics require that the bed as a whole should be designed to accept bars approx. equal in length to the bed. This cannot always be achieved, particularly when a wide range of sections and rolling speeds is employed, but there are many beds in use today on which full-length bars are regularly handled.

Mechanical beds using notched bars are the only certain means of keeping the rolled products straight during cooling. I cannot agree that, to reduce capital cost, it is preferable to use a readily replaceable form of notch bar. It should be designed so as to minimize maintenance and replacement, thereby reducing the operating costs of the bed, and to eliminate, as far as possible, any subsequent costly cold rectification of the rolled-steel products by ensuring that the notches are always in perfect alignment. The shape of the notch in the carry-over bars varies, but most beds now use unsymmetrical notches suitable for conveying sections such as beams, channels, angles, and tees as well as the more normal products of bar mills.

The straightness of a bar is often lost by the mechanism of the throw-off gear deflecting under load, and straightening pockets are necessary to rectify this on beds on which the bar is transferred while still in forward motion. One or, at the most, two straightening pockets are adequate for this purpose. If all bars can be delivered straight to the run-in table and brought to rest before discharge, straightening pockets are unnecessary, and such bars can be transferred direct to the main cooling section. The number of straightening pockets used is governed by the type of product rolled and the size and shape of pocket used. If the round bars are small the impact against the abutment face after rolling down one incline will give sufficient straightness. For heavier rounds a second straightening pocket may prove beneficial.

* C. L. Raisig, *Proceedings of the Association of Iron and Steel Engineers*, 1945, pp. 579–589.

The pack-annealing mechanism shown in Fig. 8*b* and other similar devices do not cause the bars to sweep when cooling. The rate of heat-loss through the iron castings on which the pack rests is presumably approximately equal to the radiation losses from the upper surface, although I have no authoritative figures. Should such sweeping of the bars occur, the mechanism for flat packing (Fig. 9*c*) will minimize this tendency.

The temperatures from which Fig. 15 was compiled were obtained under normal operating conditions for each type of bed. In most cases contact pyrometers were used at various positions on the bar as it moved across the bed from the straightening pocket to the shuffle bars.

The curves shown in Fig. 14 were based on hypothetical considerations and cannot be assumed correct for every type of bed or set of operating conditions. For instance, the cooling rate of $\frac{3}{4}$-in. dia. rounds (Fig. 15*e*) and of sections in other diagrams having about the same W/A ratio differ from the examples given by Mr. Hood. All the diagrams except Figs. 15*c* and *d* refer to notch-bar beds on which the bars are spaced at fixed centres, regardless of size or rate of mill output. Figures 15*c* and *d* refer to roller-type beds on which the bars can be spaced to best advantage. The rate of heat-loss due to radiation and natural convection varies with the distance between adjacent hot bars.

The bed to which Figs. 15*c* and *f* refer had a pack-annealing mechanism similar to that shown in Fig. 8*b*, but in the tests this was used only as a simple transfer device.

Figure 18 was based solely on values given by Raisig for a single-sided bed of a type, size, location, and duty similar to that required for the mill layout in Fig. 1*b*.

Mr. **H. C. White** (The Park Gate Iron and Steel Co., Ltd.): All the cooling beds illustrated in this paper are of either American or Continental design. Although we have seen examples of the Morgan bed in this country, many of us know the other types described only by photographs seen in the technical press.

The carry-over elements in Fig. 7 are prevented from falling sideways by the horizontal push rods, and the bed is stabilized in the longitudinal direction by cross slides bolted to heavy concrete blocks as shown in Fig. 8*c*. With the bed in operation the main girders supporting the carry-over elements will expand, and being restrained at each end by the cross slides the bed will presumably hump unless this expansion is absorbed by other means not shown. Does humping actually take place, and, if so, is it so negligible as not to affect the straightness of the bars?

Is each roller in the double-sided bed in Fig. 7 driven independently or is the motor double-ended, with rollers fitted at each side? Difficulty has been experienced with drives of the latter type, as it is not easy to remove and replace the motor and two rollers as a unit.

Figure 4 is made up from calculations based on the coefficient of friction between hot steel and smooth machined cast iron. In practice there is little variation in the length of slide from one bar to the next. The leading ends of bars line up very closely and the maximum variation of 5–6 ft. is surprising in view of the delivery speed.

Although Mr. Udall deals with the operation of the pack-annealing feature for spring flats shown in Fig. 8*c*, no mention is made of the method used for bringing the retractile support to the top of its stroke when the first pack is to be started, nor for providing some resistance to downward movement. In certain examples, a motor-driven line-shaft, running the full length of the bed, is apparently provided. Each retractile support is connected to this shaft with a thin wire rope, which makes 1 or 2 turns around the shaft, the free end carrying a tension weight. As the retractile supports are closely spaced many ropes are required in a bed more than 400 ft. long, and replacement of broken ropes becomes a major item of repair. Has this feature now been improved?

Figure 8 shows that the apron plate and the side guard are cast in one unit. All these castings are associated with a lever and spring connected to a power-operated gear. Are the springs in compression when the apron plate is down and is their function to lift the apron plate, the power of the motor being used only to pull the apron plate down again?

In Fig. 8*c* the side guards cannot be used for kicking off the bar, this operation being performed by the crank-operated arms. In examples I have seen, these arms were made of thick-walled tube, many being badly out of alignment. Has this feature been discarded in later beds?

On p. 270 Mr. Udall states that when a pack of flats has been completely built up the retractile support disappears, allowing the leading flats to collapse. The use of the support is presumably then discontinued and as successive pieces are delivered on the hot side of the pack the flats on the opposite side are pushed on to the carry-over elements which transport them across the bed. I have seen one plant in which the transfer on to the carry-over elements is not made evenly, the flats become crossed, and difficulty is found in getting them on to the run-out table.

If the bed is very long the drive of the carry-over element lifting mechanism is duplicated and interconnected. A brake is necessary to stop the carry-over elements in their proper relative positions. How are these two motors interconnected electrically, so that if one motor fails, the full load does not come on to the remaining one? What ensures that the remaining motor does not also have to overcome the resistance of the brake of the other?

There is a difference of opinion amongst operators as to which is the most successful type of time-delay switch for initiating the kick-off gear. Is it true that there is no completely successful type?

One bed I have seen has a throw-off gear of a type not described by Mr. Udall. The run-in rollers are provided with a rather larger taper than usual, the apron plates being made to suit. All apron plates are hinged on the leading edge, so that when lifted about the hinge they not only act as a brake to the motion of the bar but, their trailing edges being lower on the cooling-bed side, the bar is thrown off into the straightening groove. What are the disadvantages of this arrangement, which functioned very well?

Mr. **W. Udall**: The carry-over cooling section of the cooling bed in Figs. 7 and 8 is made in 15-ft. lengths, one end of each being located longitudinally by sliding plates. Adjacent ends of each pair of lengths have the plates close to each other (*see* Fig. 8*c*). Thermal expansion is therefore limited to a 15-ft. length, which even at the high temperatures experienced on cooling beds does not prove troublesome; buckling or humping of the bed does not arise. Care must be taken, particularly around the run-in table and bar throw-off gear area, to ensure an adequate number of slip points and their proper location, to prevent jamming of the mechanism. On very long beds I have seen complete sections pushed as much as 2 in. out of line by faulty design or manufacture.

The double-sided bed shown in Fig. 7 uses individually driven rollers, pitched at 3-ft. centres on each table, which is 1 ft. 6 in. staggered pitch for the twin tables. Any single motor and roller can therefore be removed easily, although the temperature around the run-in table

will make the removal of a roller unit uncomfortable, particularly if the other half of the bed is in use. It might be more difficult to remove a motor driving two rollers, one on each end of the rotor shaft, but it is not impossible. If preventive maintenance is practised it will rarely be necessary to remove a unit during a mill run.

On most beds in use today successive bars can be positioned so that the leading ends line up fairly uniformly. The equipment controlling this is sufficiently stable for an occasional bar to be thrown a few feet out of line by its use to facilitate the removal of a sample piece.

Mr. White's additional information on the pack-annealing mechanism (*see* Fig. 8*b*) is accurate. Wire ropes holding the retractile dogs are a form of drive still in use and have presumably given little trouble, so that rope breakages, if any, are unimportant. The packs of flats formed do not always break evenly at the discharge end and fall in an orderly manner on to the carry-over cooling elements, so that manual assistance is sometimes required. It is very difficult to hold a flat on edge and keep it perfectly straight over a length of say 300 ft.; the mechanism shown in Fig. 8*b*, although not perfect in operation, is the best yet devised.

The springs of the apron-plate lifting mechanism shown in Fig. 8*b* are used to partially counterbalance the dead weight of the apron side guards and the supporting mechanism. The main driving motor is therefore used to overcome the out-of-balance load and to actuate the bar sweep-off gear. The example of the bar throw-off gear to which Mr. White refers is that installed on the bar mill of the Great Lakes Steel Company. Some trouble was experienced with this bed because the bars struck and distorted the sweep-off arm during discharging and before the forward motion of the bar had been fully arrested. This trouble was largely overcome by fitting to the upper end of the sweep-off arms shoes specially shaped to deflect the oncoming bar in front of the arm.

On long cooling beds a two-motor drive is often used for the carry-over elements. The two motors can be cross-coupled to keep them in step electrically, and are mechanically tied together through a long shaft. As dynamic braking is used, one magnetic brake is sufficient to serve both motors. If one motor fails the other will not have to overcome the resistance of the brake. The type of bed shown in Fig. 7 is a balanced unit, with all the cooling elements moving and adjacent carry-over bars moving in opposition to each other. Thus the drive motors are used to overcome inertia rather than dead load. On the longest beds one motor of the normal size is adequate for this duty, two motors being used solely to reduce the deflection in the long shafts resulting from a one-motor drive.

Mr. White largely answered his point about the accuracy of the time-delay switches for initiating the bar throw-off gear when he said that he had seen successive bars line up regularly on the carry-over cooling elements. I can give no factual information about the reliability of such time-delay switches, but most cooling-bed operators would confirm that these switches are fairly reliable, provided preventive maintenance is carried out.

The type of bar throw-off gear known as Noll plates functions excellently, but as the plates rise about a fulcrum point to throw the bar off the table, successive bars slide mainly on the trailing edge of the plates, and grooves are soon worn into them. These grooves ultimately prevent the bar from rolling freely into the straightening pocket. Moreover, as all the plates rise in unison they form the series of abrupt inclines over which the leading end of the bar must travel until it is discharged. These inclines cause the bar to gallop and may cause occasional cobbles.

Mr. **R. Stewartson** (The United Steel Companies, Ltd.): Can Mr. Udall suggest a simple and cheap cooling bed for the many small hand-type mills existing today? We are economically limited for that type of mill to the gravity cooling bed.

The type of cooling bed mentioned by Mr. Hood was one built by Sack; when the shear made its cut, the front of the second bar length did catch up with the back of the first length.

Is the effectiveness of straightening pockets related to a particular size range; would large rounds above 2 in. be effectively straightened by any type of pocket?

A simple solution to the troubles experienced with the skew-roller bed which the author describes would perhaps be to mount some spiral guide, such as an Archimedes screw, on the rollers, together with a positive bevel-gear drive. This should result in straight products, although rubbing, which would spoil the appearance of the bars, might occur.

The method of moving the carry-over racks on the type of bed shown in Figs. 7 and 12 seems more complicated than that on the Edward's bed. What are the advantages of the former method, and is it more expensive?

In Fig. 8, the run-in rollers are shown mounted on an overhung shaft. Is there a size limit for bars which can be carried, particularly on double runouts with overhung rollers on each side? Would the roller shafts bend with heavy bars and lead to rubbing between the stator and rotor of the driving motor, which may be designed with small clearances? Special precautions should be taken in the design of the motors, particularly as the example quoted has a wide speed range of 5 : 1; at the lower speeds, which presumably apply to the heavier sizes of bar and the maximum torque, the insulation of windings is very important. Would it be possible to have a vee-belt drive to these rollers, of the type widely used on the Continent, although not in this country?

When rolling alloy steels it is important to use the cooling bed as a rapid transfer, so that the bars can be sheared hot. Can the author describe the equipment available for keeping the product straight after shearing, when still hot and perhaps above the so-called stiffening temperature?

Figure A, in which the experimental cooling rates are compared with the theoretical cooling rates, shows the latter to be sufficiently accurate for final temperatures between 170° and 190° F. A difference of 20° F. at the final stage represents a large time interval, evident from Fig. 14, and a significant proportion of the cooling time. A better idea of the accuracy of the theoretical calculations would be given by measuring the cooling time from, say, 1600–400° F., where the slope of the cooling curve in Fig. 14 is still fairly steep, rather than down to 180° F., where the curve is flat.

Mr. **W. Udall**: I do not know of any simple and cheap cooling bed economically justifiable for the many small hand-type mills in use today. There is not, as yet, a solution which compromises between the gravity bed shown in Fig. 2 and the simpler, but nevertheless expensive, beds briefly described in my paper.

I have no doubt that the rolling-mill plants in which the flying shear is located close to the cooling bed, and on which successive cut bars overtake each other on the bed run-in table, satisfy the user for his particular class of steel and type of product, but this practice would not be acceptable in all plants. Plant builders today have to produce equipment to handle a wide variety of sections so as to ensure that they arrive in the cold-finishing department in prime condition. Two pieces of

hot soft metal travelling at different speeds on the same roller table will not fulfil this condition.

I would say that the effectiveness of straightening pockets is limited to bars of up to 1½ in. dia.; to straighten a 2-in. dia. bar by impact would mean a very deep pocket.

Bevel or mitre gears have been, and are being, used to drive the skew rollers of roller-type beds. I have seen these gears located at the shuffle-bar end of the skew rollers. They are not more than 4 in. across the points of the teeth, and are contained in cast gear-cases. By this means continuous rotary motion can be imparted to the rollers. Because of their small size, the gears might need considerable maintenance.

Roller-type beds using Archimedian screws have been built by an American firm for conveying hot tubes. These rollers are set at right angles to the table, alternate rollers rotating in opposite directions and also having the helix angle of the Archimedian screw opposite. They are satisfactory for handling tubes, and no doubt also for handling heavy round bar, although I know of no case where they have been applied to bar mills. I doubt whether they would be suitable for handling non-rollable sections or for small rounds which may be prevented from rolling by the sag between adjacent supports. The flank and body of the screw would rub against the rolled section, which will ultimately damage the surface of the product.

The mechanism for moving the cooling elements of the bed shown in Fig. 7 is more elaborate and more costly than that shown in Fig. 3, but it is more flexible and is designed for duties not required from plants on which a cooling bed such as that shown in Fig. 3 would serve. The carry-over drive in Fig. 3 is simple, relatively trouble-free in operation and is suitable when only fixed-pitch working is required. The mechanism shown in Figs. 7 and 12 was originally devised for handling, among other things, a wide variety of section shapes and weights and also alloy steel. These require variable-pitch movement of the carry-over cooling elements, according to the size and complexity of the section and the thermal treatment required by the steel. By adjusting the movement of the flat-faced carry-over bars, any size of flat or rim bar or any shape of unbalanced section could be packed edge to edge to minimize cambering, and any other shape could be spaced to give the desired rate of cooling.

To adjust the pitch of movement a lever of adjustable length was incorporated between the drive and the rocking mechanism, giving an infinite variation within the limits of the design. Later developments showed that this variation is rarely necessary and the design has now been modified to add a limited number of set pitches to the fixed pitch setting for the notch bars.

The overhung roller table and motor, whether of the single- or double-sided type, is adequately strong in practice and I know of no case of recurring damage to the motor shafts, which for most beds are about 1 in. or 1⅛ in. dia. The motor rotors run in ball or roller bearings and the windings are protected by special insulation for the high-temperature working conditions. I would limit the bar size on this type of table to 2½-in. dia. or the equivalent.

The speed range of 5 : 1 quoted for run-in tables is necessary to meet the range of delivery speeds on modern bar mills, which is usually 3 : 1, and sometimes 4 : 1. At the lower end of the speed range the table and mill speeds must match for the individual heavy-weight bars; at the higher end the table speed must be greater than the mill speed to accelerate the successive cut lengths from the shear.

Vee-belts or ropes are not suitable for driving the run-in table rollers of modern single-sided cooling beds. Ropes were used when beds were relatively short and outputs comparatively small. On the modern bar mill cooling bed, leather or composition belts would become brittle under the high temperatures, and the fluctuating and heavy loads would cause frequent failure. Vee-belts are popular on the Continent but I have no information about their success. Experience in this country and in the U.S.A. has presumably shown this type of drive to be unreliable in operation.

Various cooling beds, and particularly that shown in Fig. 7, can be used as hot transfers to allow alloy steels to be sheared hot. The type of equipment for keeping the bars straight after shearing and beyond the bed could only be determined if the particulars of the section, the qualities of the steel, the method of handling, and the subsequent treatment are known.

The figures given in Fig. *A* are only approximate, because precision instruments were not available when the tests were made. The additional cooling information required by Mr. Stewartson can be calculated. In my calculations I have made the following assumptions:

(i) Heat loss due to conduction is negligible;
(ii) Forced convection is not used; and
(iii) The temperature within the metal is constant.

Thus all the heat is lost by radiation and natural convection.

Symbols used:

Q = Heat lost in B.Th.U.
h = Rate of heat loss in B.Th.U./hr./sq. ft. of surface area/° F. temp. fall
t_s = Surface temp. of metal, °F.
t_a = Ambient temp., °F.
S = Specific heat
W = Wt. of bar, lb.
A = Surface area of bar, sq. ft.
θ = Time, hr.

Heat lost from surface =

$$\delta Q = hA(t_s - t_a)\delta\theta \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Heat lost from steel =

$$\delta Q = WS\delta t \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$\therefore hA(t_s - t_a)\delta\theta = WS\delta t$$

$$\frac{hA}{WS}\delta\theta = \frac{\delta t}{t_s - t_a}$$

Then integrating for the whole bar, but for a small temp. range $(t_1 - t_2)$, so that h and S may be assumed constant, we have:

$$\frac{hA}{WS}\theta = \log_e \frac{t_1 - t_a}{t_2 - t_a} \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where t_1 = initial surface temp., °F.
and t_2 = final surface temp., °F.

Thus the duration of cooling θ is directly proportional to the ratio W/A.

The rate of heat loss is

$$h = \frac{1730E\left[\left(\frac{T_s}{1000}\right)^4 - \left(\frac{T_a}{1000}\right)^4\right] + C(t_s - t_a)^{1.25}}{t_s - t_a}$$

The shape factor in Stefan Boltzmann's law has been ignored and the emissivity factor E has been taken as 0·8, which is within ± 15% of any variation. The constant of convection C varies considerably according to shape and size, but an average value of 0·4 has been assumed. Inaccuracies arising from this assumption do not seriously affect the results in the higher temperature range as shown by Fig. 16.

$$\frac{W}{A} \text{ for a round section} = \frac{S \times l \times \frac{\pi}{4}d^2}{l \times \pi \times d} = \frac{Sd}{4} \quad \ldots\ldots (4)$$

$$\frac{W}{A} \text{ for a rectangular section} = \frac{S \times l \times b \times t}{l \times 2(b + t)}$$

$$= \frac{Sbt}{2(b + t)} \quad \ldots\ldots\ldots\ldots (5)$$

Equating (4) and (5),

$$d = \frac{4bt}{2(b + t)}$$

$$i.e., \text{ equivalent round} = \frac{4 \times \text{cross-sectional area}}{\text{length of periphery}}$$

where l = length of bar
d = dia. of round bar
b = breadth of rectangular bar
t = thickness of rectangular bar.

Mr. **B. Robinson** (Park Gate Iron and Steel Co., Ltd.): Figure 4 shows that with a run-in table speed of 2200 ft./min. the bar will slide about 100 ft. In one case, the bar slides against the faces of the straightening pocket, but it slides in another type of bed against the surfaces of the apron plates. Is there a danger of the bar surface being damaged in this way, and if so are any precautions being taken to prevent such damage?

Mr. **W. Udall**: The two main methods of arresting the forward motion of a bar are described in my paper and are shown in Figs. 3 and 7. The equipment shown in Fig. 3 discharges the bar from the run-in table into the straightening pocket while still travelling at full speed and, provided there are no projections on the faces of the straightening pockets, it slides to rest with little or no danger of surface damage. The apron plates in Fig. 7 are lifted above the level of the table rollers to arrest the forward motion of the bar wholly or partially before it is discharged into the straightening pocket. As the apron plates are machined on the upper surface the danger of marking or scratching is very slight. When one metal slides over another the possibility of scratching is always present and care should be taken to ensure that surfaces in contact with the bar are smooth and unbroken. The faces of the straightening pockets should be machined and in perfect alignment.

Mr. **M. Langen** (Loewy Engineering Co., Ltd.): The paper does not deal sufficiently with the latest designs of roller cooling beds. I believe that the bed shown in Fig. 5 is obsolete; an up-to-date design of an automatic roller cooling bed incorporates many improvements and has proved a very efficient finishing-end for merchant mills of either the continuous or semi-continuous type, rolling bars up to 1½ in. or equivalent sections.

A modern one-sided automatic roller cooling bed fulfils the requirements given by Mr. Udall: it receives two bars simultaneously but separately and transfers them individually across the cooling bed to the cold shear without causing a bottleneck in the mill output. Such a cooling bed has a run-in trough with two partitions, one for each strand. That part of the aprons between the individually driven rollers can be lifted to bring the bar to rest before it is transferred to the first portion of the cooling bed proper. Such an ejector system has the advantage that the gap between successive bars can be kept very small, and the rotary shears can be placed about 50 ft. away, even for mill speeds of 2100 ft./min. This distance is necessary to bring the bar to rest with its tail flush with the beginning of the cooling bed.

The bar when lifted is supported over almost its whole length, and when being side-transferred its individual movement is restricted to a minimum, thus avoiding twist, which may be very important. The first part of the cooling-bed surface consists of cast-iron aprons with 10–18 notches or pockets into which the bars are placed step-wise by closely pitched racks similar to those used for the carry-over type cooling bed. These pockets fully support the bars, which are cooled sufficiently before they reach the skew rollers that form the second part of the cooling-bed surface. This gives a highly desirable straightening effect and avoids the deformation of even small bars when placed on the skew rollers.

Two cold shears are usually desirable for a single-sided cooling bed, and should be placed at a distance from the bed equal to at least half the length of the latter. However, since a cooling bed for a merchant mill should have a minimum length of, say, 230 ft. to avoid too much scrap, a very long bay is required. Site conditions do not always allow for such a length, and designs have therefore been developed using only one shear, situated at the end of the cooling bed. In such cases I prefer a carriage between cooling bed and cold shear which lifts a batch of bars before the preceding batch has been sheared, allowing the next batch to proceed underneath the carriage. When the cold shear is ready the lifted batch can be transferred to the roller table more quickly, thus reducing the idle time of the cold shear.

An up-to-date cold shear is a very efficient unit, having a 34-in. blade capable of cutting many small bars simultaneously. When cutting a minimum length of 30 ft. such a shear can deal with a mill output of 60 tons/hr.; the output is increased when bars of ⅜ in. and greater are being rolled. If the loading pockets cannot be placed beyond the shear stop gauge, the shear can be arranged so that the cut-off bars can be side-transferred into pockets without being moved away from the shear, which again speeds up the shearing operation. Whenever possible four loading pockets should be provided to facilitate bundling and weighing.

Mr. **W. Udall**: I have not seen a recent installation of a modern version of the roller-type cooling bed described by Mr. Langen. The roller-type bed shown in Fig. 5 might be considered obsolete as it was built almost two decades ago, although it is still operating to the satisfaction of its owners.

Mr. Langen mentions that the up-to-date design of roller cooling beds contains cast-iron aprons with 10–18 notches or pockets into and across which the bars are conveyed step-by-step immediately after their discharge from the run-in table. I suggest that as carry-over type cooling beds have 16–22 pockets including the straightening pockets, Mr. Langen is really describing not a roller-type cooling bed but an orthodox carry-over type bed, the cooling capacity of which is extended by skew-roller elements. To use skew rollers for secondary cooling will involve a capital outlay that may not be justified, as this can be done almost as efficiently and certainly more cheaply by extending the shuffle bars as shown in Fig. 7 and as described in my paper.

I agree with Mr. Langen's comments about the cold shears following the cooling bed, but it is very short-sighted to condense a high-output plant into the minimum of space. If site conditions permit, each unit in a plant should be so located that its capacity can be fully used. If in the case of the cold shear this is impossible, a bar-handling mechanism should be used to feed the shear. A variation of the mechanism shown in Fig. 13 could, and has been, used in this capacity.

Where one shear only is used there is a danger of mill hold-ups, irrespective of the efficiency of the shear as a whole. Breakdowns occur and shear blades require changing, and this cannot always be done before the bed becomes fully loaded. When this happens the mill production must be slowed down and ultimately stopped until the shear is put back into commission.

Four bundling stations are desirable to deal with high rates of output, and although efficient side-transfer units are available for clearing the shear run-out table, the cut lengths should wherever possible be run out beyond

the gauge head before being removed from the table. A simple time study shows that side-transferring of bars entails more time than direct run-out, and where one shear only is used this extra time could affect the overall output of the plant.

Mr. **N. R. D. Gurney** (Metropolitan-Vickers Electrical Co.) : On p. 273 the author mentions synchronizing the peripheral speed of the table rollers with that of the last stand of the mill, the rollers being individually driven by small squirrel-cage motors supplied from a variable-frequency motor generator set. To achieve synchronization the D.C. variable-speed motor driving the variable-frequency motor generator set should be supplied from the same power supply as the delivery-stand driving motor.

This method may be practicable only in a few cases because, apart from starting and stopping, the mill-speed variation is normally obtained by field weakening of the mill motors. This is because the highest mill speeds are generally required for the smallest sections rolled, which in turn require the lowest torques, and *vice versa—i.e.*, a substantially constant h.p./speed characteristic is required of the mill motors. This is obtained by varying the field strength of the motors and not the voltage applied to the motor armatures.

Another method is to drive the variable-frequency alternator supplying the table motors from the motor driving the delivery stand on the mill so that the alternator speed and frequency is proportional to the mill-motor speed. Another method sometimes employed is to couple a tachometer generator to the delivery-stand motor and another to the shaft of the variable-frequency motor generator set, and, by means of one of the well-known control systems utilizing a metadyne, amplidyne, or other form of quick-acting exciter, to synchronize the motor-generator-set speed with that of the delivery-stand motor. Alternatively, to synchronize the table motors with the shear, a tachometer generator can be coupled to the shear-motor shaft and the control easily transferred from the last stand motor to the shear motor.

Is there an installation in this country using contact rollers as an alternative to flag switches for initiating the cycle of automatic operation ?

Mr. **W. Udall** : The alternative methods Mr. Gurney has suggested are most satisfactory for synchronizing the table speed with the speed of the delivery stand of the mill. To synchronize the table and stand speeds exactly I would recommend a magnavolt or equivalent control scheme to speed-match the VF alternator set with the driving motor of the last stand.

On the type of mill and bed we are discussing, accurate speed-matching between table and delivery stand is, however, rarely, if ever, necessary. The table speed has to vary between that approximate to the mill speed for heavy-weight bed-length bars and one considerably in excess of the mill delivery to create the gap between successive cut lengths from the flying shear. The simplest way of controlling the run-out table speed is therefore to use a rheostat in the mill pulpit and to compare the table and mill-stand speeds by indicators. The rheostat controls the field of the motor driving the VF alternator set. This simple hand control avoids the expense of an extra generator, which special speed-match control would require, and also avoids a somewhat complicated control scheme.

The driving motor of the VF set can be supplied from two sources, the constant voltage D.C. supply or the main mill bus. Economically there is not much difference, but supply from the main bus has the advantage that once the mill has been adjusted any variation of the mill speed as a whole by voltage control also varies the speed of the run-out table. This system is the most popular method in use today of relating run-out table speed to mill speeds.

The regulations in this country do not allow motors to be insulated from earth and so contact rollers are not used. They are used, however, in the U.S.A., and several cooling beds in that country use them to initiate bed operations, to the satisfaction of the operators.

Mr. **S. K. Dean** (B.I.S.R.A.) : The author uses 0·2 for the coefficient of friction, but I suggest that this varies considerably, depending on the sliding velocity. Experiments recently carried out with hot steel on a cold steel surface suggest that the coefficient of friction is about 0·35 until the sliding velocity reaches 3 ft./sec., and then it goes down very rapidly to 0·15 with a sliding velocity of 5 ft./sec. or more.

Mr. **W. Udall** : The coefficient of friction of 0·2 was found by practical tests on existing cooling beds and, while not exact for all conditions, is the lowest coefficient obtained. As the length of slide varies inversely with the coefficient of friction this figure must be taken if the bed is to be used to the best advantage.

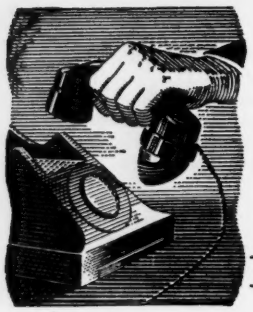
The **Chairman** : Is the cooling bed of the roller type not so satisfactory from the point of view of the surface finish of its products ?

Mr. **Udall** : If a bar of $\frac{5}{8}$ in. dia. or less is deposited on skew rollers at a 10-in. pitch, it will sag between the points of support. If this sag is appreciable the bar will not roll freely in its passage across the skew rollers and friction between the skew rollers and the bar will occur, which may damage the surface of the bar. This is even more likely to occur with flats, squares, or other sections which do not roll. Great care is taken to minimize this friction by machining the skew rollers to obtain a smooth polished surface but this does not eliminate friction caused by the differential in speed of the roller surface and the material that it supports.

This rubbing action may not be serious except in cases where surface finish and quality are important.

Mr. **M. Langen** : If a modern roller cooling bed is combined with a rack-type mechanism, the bar is sufficiently cooled down and mostly black when being placed on the skew rollers. In this case there is no deformation and I have seen $\frac{1}{4}$-in. bar without deformation on the skew-roller bed.

Mr. **Udall**: If the bar is black-cold before it is deposited on the skew rollers, any size down to $\frac{1}{4}$-in. dia. will be adequately supported and will probably roll in its passage across the skew rollers. Most roller-type cooling beds today have no primary cooling racks, and those that have are generally limited to two, four, or at the most six notches. Thus most bar sizes rolled will be deposited on the skew rollers while still in a soft state and sagging between the points of support may occur. If substantially flat products are deposited on the skew rollers, friction is bound to occur and the surface may be scratched. Whether this is detrimental or not depends entirely on the customer's requirements.



N E W S

ANNOUNCEMENTS AND NEWS OF SCIENCE AND INDUSTRY

THE IRON AND STEEL INSTITUTE

Autumn General Meeting, 1952

The **Autumn General Meeting** will be held in London on Wednesday and Thursday, **26th and 27th November, 1952.**

Changes on Council

The following changes were announced at the Annual General Meeting held on 30th April, 1952 :

Mr. C. R. WHEELER, C.B.E., has been nominated a Vice-President

Mr. B. CHETWYND TALBOT has been elected a Member of Council

The following have accepted invitations to serve as Honorary Members of Council during their periods of office :

Dr. C. J. SMITHELLS, President of the Institute of Metals

Mr. E. TAYLOR-AUSTIN, Chairman of the North Wales Metallurgical Society

Mr. H. ALLISON, President of the Manchester Metallurgical Society

Mr. W. REGAN, President of the Staffordshire Iron and Steel Institute

NEWS OF MEMBERS

▶ Mr. G. L. BAILEY, Director of the British Non-Ferrous Metals Research Association, has been elected a Vice-President of the Institute of Metals.

▶ Mr. A. J. BLANCHARD has transferred from the Plant Engineering Division of the British Iron and Steel Research Association to become Assistant Mechanical Engineer in the Iron Making Division at the North East Coast Laboratories, Normanby.

▶ Dr. S. F. DOREY, Chief Engineer Surveyor of Lloyd's Register of Shipping, has been elected a Vice-President of the Institute of Metals.

▶ Lt.-Col. FRANK H. HOLMES has transferred from the North Atlantic Defence Production Board in London to take up an appointment with the North Atlantic Treaty Organization in Paris.

▶ Mr. M. D. JEPSON has left the staff of Messrs. Hadfields Ltd., Sheffield, to take up an appointment with the Ministry of Supply Atomic Energy Division, Salwick, Nr. Preston.

▶ Mr. G. LITTLEWOOD has left David Brown and Sons (Huddersfield) Ltd., to take up an appointment with the British Iron and Steel Research Association in Sheffield.

▶ Mr. J. WARING has been appointed Lecturer in Metallurgy in the Mining Engineering Department of the University of Queensland, Brisbane, Australia.

▶ Mr. D. K. WORN has left the English Electric Co., Ltd., Stafford, to take up an appointment in the Mond Nickel Research Laboratories, Birmingham.

▶ Mr. F. V. WRIGHT has acquired the Designing and Tracing business of Messrs. Lawes, Neal and Company, which is now to be called the Midlands Industrial Design Co., Wednesbury, Staffs.

Obituary

Dr. D. H. DRANE, of Wigan, formerly of Industrial Distributors, Ltd., Johannesburg, on 5th April, 1952.

Mr. W. T. JONES, of Port Talbot, Glamorganshire, in November, 1951.

Mr. F. E. REASON, of Cardiff, on 8th March, 1952.

CONTRIBUTORS TO THE JOURNAL

S. E. Hadden, A.I.M.—A member of the staff of the corrosion section of the British Non-Ferrous Metals Research Association. Mr. Hadden was educated at Alleyn's School, Dulwich, and at Battersea Polytechnic. His main work has been on the corrosion of zinc and galvanized steel and on the corrosion (including stress corrosion) of light alloys. He joined the Research Association in 1938.

S. E. Hadden

A. Goodall—Senior Assistant in the Steelworks Section of the Metallurgical Department of the Appleby-Frodingham Steel Co., Scunthorpe.

Mr. Goodall was born in Gainsborough, Lincolnshire, in 1913, and was educated at Gainsborough Grammar School. In 1929 he joined the Appleby Melting Shop of the Appleby-Frodingham Steel Co. as a shift chemist, and subsequently transferred to the Metallography Research and General Analysis Sections of the Laboratories. Recently he has been engaged on the application of systematic training methods to staff observers, for the purpose of obtaining accurate and consistent metallurgical data on the making and rolling of semi-killed ingots. He has held his present position since 1940.

R. Wogin, B.Sc.(Lond.), A.Met.(Sheff.), A.I.M.—Manager of the Appleby Melting Shop of the Appleby-Frodingham Steel Co., Scunthorpe. Mr. Wogin joined The United Steel Companies, Ltd., in 1935, under their Student Apprenticeship Scheme. He was a scholarship student at Sheffield University for two years, where he was awarded the Associateship in Ferrous Metallurgy in 1939. He obtained his B.Sc. (External) degree at London University in 1940. Since then he has been engaged on open-hearth steelmaking in large tilting furnaces.

A. Goodall

R. Wogin

In 1950 Mr. Wogin spent six months in Australia, America, and Canada, studying the steelmaking techniques of these countries under an exchange scheme between The United Steel Companies and the Broken Hill Proprietary Company of Australia. While in America he visited 13 of the leading steel mills, from Fontana on the west coast to Sparrows Point on the east.

AFFILIATED LOCAL SOCIETIES

Cleveland Institution of Engineers

Under the terms of the Will of the late Mr. T. H. W. Chambers a sum of fifty pounds was left to the Cleveland Institution of Engineers to encourage younger members to submit Papers.

The Council have decided to award annually a prize of ten pounds (in books or cash) for the best Paper, on a subject acceptable to the Institution, which is submitted by a Member who is not more than 30 years of age on the 31st day of December in the year in which the Paper is submitted.

Applications for permission to submit a Paper should be made on the official form, copies of which may be obtained from the Honorary General Secretary, Mr. F. G. E. Webster, 5 Ambleside Road, Normanby, Middlesbrough.

North Wales Metallurgical Society

The North Wales Metallurgical Society has become affiliated to The Iron and Steel Institute. The Chairman, Mr. E. Taylor-Austin, F.R.I.C., F.I.M., has been invited to become an Honorary Member of Council of the Institute during his period of office.

The Honorary Secretary of the Society is S. Weir, Esq., 67 Wepre Park, Connah's Quay, Nr. Chester.

EDUCATION

National Certificates In Metallurgy

REPORT BY THE JOINT COMMITTEE ON THE PROGRESS OF THE SCHEME FOR THE AWARD OF NATIONAL CERTIFICATES IN METALLURGY FOR THE YEAR 1950–1951

The Joint Committee has approved eleven new Schemes for National Certificates in Metallurgy during 1951, and Schemes are also being organized in districts not yet covered, with a view to suitable courses being started as soon as possible.

The content of a Scheme for a Senior Course in Metallurgy, submitted by the Welsh Joint Education Committee, has been agreed as suitable for submission by Colleges in Wales, in connection with their applications for approval of Senior Courses in Metallurgy for the purpose of Ordinary National Certificates.

Courses approved by the Joint Committee have been in operation during 1950–1951 at the following Technical Colleges :

Ordinary National Certificate—Birmingham College of Technology ; Bristol, The College of Technology ; Chesterfield Technical College ; Corby Technical College ; Coventry Technical College ; Crumlin, The Technical College of Monmouthshire ; Cumberland Technical College, Workington ; Derby Technical College ; Enfield Technical College, Middlesex ; Leeds College of Technology ; Llanelly Technical College, Carmarthenshire ; Manchester College of Technology ; Middlesbrough, Constantine Technical College ; Neath Mining and Technical Institute ; Newcastle-upon-Tyne, Rutherford College of Technology ; Newport Technical College, Monmouthshire ; Nottingham and District Technical College ; Preston, Harris Institute ; Rotherham College of Technology ; Scunthorpe Technical College ; Shotton, Deeside Technical Institute ; Smethwick, The Chance Technical College ; Stoke-on-Trent, North Staffordshire Technical College ; Swansea Technical College ; Wandsworth Technical College, London ; Wednesbury, County Technical College ; Wolverhampton and Staffordshire Technical College.

Contributory Centres—Bordesley Green Technical School, Moseley Grammar School Evening Institute, and Kidderminster School of Science (Contributory Centres to Birmingham College of Technology) ; Dudley and Staffordshire Technical College (Contributory Centre to Wednesbury, County Technical College) ; Nottingham People's College Senior Technical Institute (Contributory Centre to Nottingham and District Technical College) ; Wolverhampton, Wulfrun College of Further Education (Contributory Centre to Wolverhampton and Staffordshire Technical College).

Higher National Certificate—Battersea Polytechnic, London ; Birmingham College of Technology ; Chesterfield Technical College ; Coventry Technical College ; Cumberland Technical College, Workington ; Middlesbrough, Constantine Technical College ; Newport Technical College, Monmouthshire ; Nottingham and District Technical College ; Rotherham College of Technology ; Scunthorpe Technical College ; Shotton, Deeside Technical Institute ; Sir John Cass College, London ; Smethwick, The Chance Technical College ; Swansea Technical College ; Wednesbury, County Technical College ; Wolverhampton and Staffordshire Technical College.

Final Examinations of the course for the Ordinary National Certificate have been held during 1951 at 25 Technical Colleges, and for the Higher National Certificate at 16 Technical Colleges, for candidates who have satisfied the conditions laid down in Ministry of Education Rules 111, under which the Scheme is operated.

134 Candidates have qualified for the award of an Ordinary National Certificate in Metallurgy, and 54 candidates have qualified for the award of a Higher National Certificate, as a result of Final Examinations held in 1951. The records of a further 9 candidates for the Ordinary National Certificate and 6 for the Higher Natonal Certificate have been approved by the Joint Committee, subject to the fulfilment of certain conditions. Four candidates for the Ordinary Certificate, who entered the Final Examinations in 1949 or 1950 and whose records were approved by the Joint Committee, subject to certain provisions, have qualified for the award of Certificates in 1951. Distinctions have been

gained by 22 candidates who have shown an exceptional grasp of their subjects, indicating a high degree of training and knowledge in the particular subject in which the Distinction has been gained.

Comparative figures of entries and successful candidates for the six years since the institution of the Scheme for National Certificates in Metallurgy are as follows :

Ordinary National Certificate

Year	Technical Colleges	Number of Candidates Entered	Awarded Certificates
1946	4	28	23
1947	11	102	69
1948	15	123	74
1949	21	222	107
1950	20	281	142
1951*	25	314	138

Higher National Certificate

Year	Technical Colleges	Number of Candidates Entered	Awarded Certificates
1946	...	...	...
1947	2	22	18
1948	8	38	22
1949	10	74	59
1950	11	62	42
1951*	16	110	54

Prizes were awarded to 35 successful candidates who showed particular merit in the Final Examinations in 1951, from the Prize Fund established for this purpose by The Iron and Steel Institute, the Institution of Mining and Metallurgy, and the Institute of Metals.

The Joint Committee takes this opportunity of thanking the Assessors for their valuable assistance in the operation of the scheme.

The following candidates successfully completed the senior part-time course for the year 1950–51 and have been awarded the Ordinary National Certificate in Metallurgy (a subject given in parentheses indicates the award of a distinction in that subject) :

ORDINARY NATIONAL CERTIFICATE

Birmingham College of Technology—Bishop, Edward Ernest ; Boulter,† Stanley Arthur ; Clewes,† David Anthony ; Clyne, John Middleton ; Coley,† Richard Ivor ; Evans, Ronald Ernest ; Farmer,† Raymond Cedric (chemistry) ; Farrimond,† Dennis Hugh ; Gabel,† Harold Harry ; Green,† Colin (chemistry) ; Holland,† Harry Raymond ; Jackson,† Geoffrey (engineering drawing) ; Jones,† Peter Edward ; Lawrence,† Trevor Ronald J. ; Priddy,† Francis Barry ; Pursall,† Francis Walter ; Ratledge,† John William ; Sumner,† Le-Roy Robert ; Taylor, Kenneth Harold ; Timmis, Albert Roy ; Wheeldon,† Peter Albert.

Chesterfield Technical College — Allwright, Jack ; Bargh, Colin ; Bird, Derek Francis W. ; Bradley, Ronald Sterland ; Brewer, Geoffrey (general metallurgy) ; Kirkland, John Geoffrey ; Marriott, Harry Vernon ; Orwin, Brian ; Taplin, John Avern ; Towndrow, Derek ; Woolley, Thomas Arthur.

Corby Technical College—Barlow, Geoffrey Thomas ; Clark, Derek Foster ; Dartnell, John (physics) ; Dickson, Michael ; Sleith, Dougald Graham.

Coventry Technical College—Dalton, Aubrey Arthur ; Goodyer, Barrie George ; Lee, John ; Mole, Paul Malcolm ; Murray, Thomas Anthony ; Wood, Gerald Arthur.

R. H. Bracewell has qualified in Mathematics S.3 for supplementary endorsement on his Certificate gained in 1950.

Crumlin, The Technical College of Monmouthshire—Bevan, Morgan ; Davies, John ; Gunter, Glyn ; Lewis, Gareth Gwyn.

Cumberland Technical College, Workington—Harle, Cyril Dawson ; Ivison, Eric (physics) ; Simpson, Norman ; Stevenson, Joseph Aidan (inorganic and physical chemistry) ; Wilson, John Raymond (inorganic and physical chemistry) ; Woodward, Rodney Michael (physics).

J. A. Stevenson and R. M. Woodward have qualified in Mathematics S.3 for supplementary endorsement on their Certificates.

Derby Technical College—Marshall, Brian Geoffrey.

Enfield Technical College—Sumerling, Roy Thomas.

Llanelly Technical College—Cooke, Paul Aldrich ; Godber, Frank ; Thomas, Dennis Bowen ; Wehrle, Michael.

Manchester College of Technology—Martin, Norman Swirles ; Whitehead, Tom.

Middlesbrough, Constantine Technical College—Boyes, Donald Anthony ; Drayton, Joseph Henry ; Knott, Ronald ; Manton, Frank ; Willis, Edwin.

Neath Technical College—Hayman, Neville ; Williams, Howard.

Newcastle-upon-Tyne, Rutherford College of Technology—Gray, Noble.

Newport Technical College, Monmouthshire—Pirie, Charles William (general metallurgy) ; Hurley, Richard Daniel ; Mathias, David.

Nottingham and District Technical College—Harris, John David.

Rotherham Technical College—Brown, Edward Raymond ; Caborn, Henry Raymond ; Cocks, Derrick L. ; Godbehere, Albert Edward ; Mace, Colin ; Marshall, Roy ; Naylor, George William ; Randall, Charles Henry ; Rhodes, George Henry ; Sweeney, Brian ; Taylor, Edward ; Wagstaff, Peter ; Wallace, Frank.

Scunthorpe Technical College—Cunningham, Thomas ; Hall, George ; Hoyle, Peter ; Major, Brian ; Mann, Kenneth ; Robinson, James Frederick (physical and inorganic chemistry).

Shotton, Deeside Technical Institute—Beddard, John Herbert.

Smethwick, The Chance Technical College—Bell, Kenneth ; Broadhurst, John Cyril Y. ; Harper, Alan George ; Hipkiss, Philip Anthony ; Homer, Stanley ; Lee, Graham Bishton ; Marshall, Gerald Stanley ; Pearson, Leslie Benjamin ; Round, John Alfred ; Rowen, Graham Meredith ; Simpson, William Ernest ; Troman, John Harold ; Wormington, Harry.

A. G. Harper, P. A. Hipkiss, G. S. Marshall, and H. Wormington have qualified for the supplementary endorsement of their Certificates in Foundry Practice, taken as an additional and optional subject. J. N. Smith and G. B. Taylor have also qualified in this subject for supplementary endorsement of their Certificates gained in 1950.

Stoke-on-Trent, North Staffordshire Technical College—Bevans, Edmund Noel ; Brandrick, Godfrey Robert ; Brown, Charles Payne ; Bryan, Harry Raymond ; Dunn, Stuart John ; Lawton, John ; Mellor, Edward John ; Rawlins, Joseph Anthony ; Sale, George (physical chemistry, physics) ; Smith, Norman (general metallurgy, physics) ; Thorley, Alan William (physics) ; Turner, Bertram ; Woodhouse, Percy.

Swansea Technical College—Cartwright, George Kenneth (chemistry, general metallurgy) ; Davies, Gerald ; Edney, William George ; James, Eurof Glyndwr ; Jones, Derek Hugh (general metallurgy) ; Jones, John Colin ; Lloyd, Geoffrey John ; McNeil, William Kenneth ;

* The results of final examinations for the Ordinary and Higher Certificate held at Wednesbury, County Technical College and at Wolverhampton and Staffordshire Technical College are not yet available.

† Candidates qualified in Engineering Drawing for endorsement on their Certificates.

Millington, Geoffrey; Quick, Billie; Taylor, Clement Hastings.

Wandsworth Technical College, London—Adams, Denis Frank (general metallurgy); Clarke, Anthony; Hall, Reginald; Hills, Ronald Frederick; Smale, Alan Colin; Stubbs, Gerald Brian; Sunderland, Joseph; Watkins, Kenneth Oliver.

HIGHER NATIONAL CERTIFICATE

The following candidates successfully completed the advanced part-time course for the year 1950–51, and have been awarded the Higher National Certificate in Metallurgy (a subject given in parentheses indicates the award of a distinction in that subject):

Battersea Polytechnic, London — Bridges, Dennis Francis W.; Cox, Anthony Hugh; Day, Joseph George; Humphries, Jean Mary; Lucey, Victor Francis; Murray, Edward John; Nabbs, Stanley William; Wood, Barrie; Woods, Arthur George W.

Birmingham College of Technology—Clare, Eric Samuel; Hughes, Donald Ernest (metallurgical analysis); Jones, Ronald Arthur C.; Reeves, Gordon Leonard; Rigby, June Curtis; Swann, Brian; Wood, Allan; Woolley, Alfred Trevor.

G. L. Reeves and A. T. Woolley have qualified in Metallurgical Analysis for endorsement on their Certificates.

The following candidates have qualified for endorsement of their Certificates gained in 1950: P. J. Bettington (non-ferrous metals and alloys); R. C. Lloyd (iron and iron alloys, II); D. N. Smith (metallurgical analysis); R. A. Storer (iron and steel production).

Chesterfield Technical College—Clayton, Alan (metallurgical analysis, physical metallurgy); Salt, Norman; Stock, Donald Calthorpe (metallurgical analysis).

Coventry Technical College—Boston, Stanley John; Ford, Ashley Gregg; Jordan, Douglas Arthur; Payne, Maurice David; Spriggs, Geoffrey Edwin.

Middlesbrough, Constantine Technical College—Hepworth, Gordon.

Newport Technical College, Monmouthshire—Cantelo, Philip John; Thompson, John Alfred; Waring, Peter.

Nottingham and District Technical College—Heawood, Colin Maurice; Hurst, Malcolm Frederick; O'Dell, Clifford Graham.

Rotherham Technical College—Allen, Peter D. (production of iron and steel); Hopper, John; Monks, John; Pallister, Donald; Timmins, Arnold; Wigfield, Kenneth; Williams, Jack.

A. Timmins has qualified for endorsement of his Certificate in Mechanical Testing and Heat Treatment, taken as an additional and optional subject.

Scunthorpe Technical College—Bray, Bernard; Teanby, Joseph Donald.

Shotton, Deeside Technical Institute—Cork, John Samuel; Sharpe, Edgar Charles; Williams, Edward John.

Sir John Cass College, London—Morgan, Clifford John.

Smethwick, The Chance Technical College—Allen, Desmond Frederick; Brookshaw, Clement William; Cheesman, George Dean; Hatcher, George Clarence; Webb, Ronald James.

D. F. Allen has qualified for supplementary endorsement of his Certificate in Manufacture and Treatment of Non-Ferrous Metals and Alloys, taken as an additional and optional subject.

Swansea Technical College—Cunniffe, Peter William A.; Rees, Arthur; Snook, Vivian Thomas J. (metallurgical analysis); Williams, John Morley.

Prizes

Prizes have been awarded to the following candidates in respect of the Final Examinations for Ordinary National Certificates in Metallurgy for the year 1950–51:

Birmingham College of Technology—Farmer, Raymond Cedric (two guineas); Green, Colin (one guinea); Jackson, Geoffrey (one guinea).

Chesterfield Technical College—Brewer, Geoffrey (one guinea); Woolley, Thomas Arthur (one guinea).

Corby Technical College—Dartnell, John (two guineas).

Coventry Technical College—Bracewell, Richard Henry (Endorsement Subject) (one guinea); Wood, Gerald Arthur (one guinea).

Cumberland Technical College—Ivison, Eric (one guinea); Stevenson, Joseph Aidan (one guinea); Wilson, John Raymond (one guinea); Woodward, Rodney Michael (two guineas).

Enfield Technical College—Sumerling, Roy Thomas (one guinea).

Llanelly Technical College—Godber, Frank (one guinea).

Newport Technical College—Pirie, Charles William (two guineas).

Nottingham and District Technical College—Harris, John David (one guinea).

Scunthorpe Technical College—Robinson, James Frederick (one guinea).

Smethwick, The Chance Technical College—Simpson, William Ernest (one guinea).

Stoke-on-Trent, North Staffordshire Technical College—Sale, George (four guineas); Smith, Norman (four guineas); Thorley, Alan William (one guinea).

Swansea Technical College—Cartwright, George Kenneth (four guineas); Jones, Derek Hugh (one guinea).

Wandsworth Technical College, London—Adams, Denis Frank (two guineas).

Prizes have been awarded to the following candidates in respect of the Final Examinations for Higher National Certificates in Metallurgy for the year 1950–51:

Battersea Polytechnic, London—Cox, Anthony Hugh (one guinea).

Birmingham College of Technology—Hughes, Donald Ernest (one guinea); Swann, Brian (one guinea).

Chesterfield Technical College—Clayton, Alan (four guineas); Stock, Donald Calthorpe (two guineas).

Coventry Technical College—Payne, Maurice David (one guinea).

Newport Technical College—Waring, Peter (one guinea).

Rotherham Technical College—Allen, Peter D. (two guineas).

Shotton, Deeside Technical Institute—Williams, Edward John (one guinea).

Smethwick, The Chance Technical College—Allen, Desmond Frederick (one guinea).

Swansea Technical College—Snook, Vivian Thomas J. (two guineas).

		£	s.	d.
Ordinary Certificate:	24 students	39	18	0
Higher Certificate:	11 students	17	17	0
	35	£57	15	0

NEWS OF SCIENCE AND INDUSTRY

Conference on Fluidization Technology

A Conference on Fluidization Technology has been jointly arranged by the Chemical Engineering Group of the Society of Chemical Industry, the Chemical Engineering Section of the Koninklijk Instituut van Ingenieurs, and the Chemical Engineering Group of the Netherlands Chemical Society, and will take place in the Connaught Rooms, Queen Street, Kingsway, London, W.C.2, on

June 12th and 13th, 1952. A visit to chemical works has also been arranged to take place on June 14th.

Further particulars of the conference may be obtained from the Honorary Secretary, Chemical Engineering Group, Society of Chemical Industry, 56 Victoria Street, London, S.W.1.

Industrial Physics Conference, 1952

The Fourth Conference on Industrial Physics, arranged by The Institute of Physics, will take place in the Royal Technical College, Glasgow, from 24th to 28th June, 1952. The subject of the Conference is "Physics in the Transport, Shipbuilding, and Engineering Industries," and there will be an exhibition of relevant instruments, apparatus, and books.

The Conference will be opened by Lord Bilsland, President of the Scottish Council. The principal speakers include Sir Andrew McCance (Chairman of the Organizing Committee of the Conference) and Sir Robert Watson-Watt.

Full particulars, forms of application for Conference membership, and tickets of admission to the exhibition, may be obtained from the Secretary, The Institute of Physics, 47 Belgrave Square, London, S.W.1.

Fifteenth Congress of the Groupement pour l'Avancement des Méthodes Spectrographiques

The Fifteenth Congress of the Groupement pour l'Avancement des Méthodes Spectrographiques will be held at the offices of the Association des Ingénieurs des Arts et Métiers, Avenue d'Iéna, Paris, from 18th to 20th June, 1952. The Congress will include a visit to the laboratories and an excursion organized by the G.A.M.S.

Fifth Conference of the British Coke Research Association

The Fifth Conference of the British Coke Research Association will be held on Thursday, June 26th, 1952, and not, as previously notified, on Tuesday, May 20th.

European Foundry Mission to America

This Mission is the largest Technical Assistance Mission which has yet been sponsored by the Organization for European Economic Co-operation, and represents European foundry interests. During a four weeks' tour of American foundries, the Mission, which comprises delegations from the principal West European countries, visited the International Foundry Congress held at Atlantic City from 1st to 7th May, 1952. Mr. John Bolton, Technical Secretary of the Research and Development Division of the British Steel Founders' Association, was appointed Secretary to the Mission.

1952 Pacific Northwest Metals and Minerals Conference

The 1952 Pacific Northwest Metals and Minerals Conference was held at Hotel Davenport, Spokane, Washington, U.S.A., from 8th to 10th May, and was arranged by the Columbia Chapter of the American Institute of Mining and Metallurgical Engineers. Subjects under discussion at the Technical Sessions included extractive metallurgy, physical metallurgy, and iron and steel making.

Changes of Address

The Export Department of the British Iron and Steel Federation has removed to Egginton House, 25 Buckingham Gate, London, S.W.1.

THE INDUSTRIAL PYROMETER CO., LTD., have removed to new offices and works at Gooch Street, Birmingham, 5.

DIARY

4th–10th June—CONGRÈS INTERNATIONAL DES FABRICATIONS MÉCANIQUES—4th International Mechanical Engineering Congress—Stockholm.

4th–14th June — Mechanical Handling Exhibition — Grand and National Halls, Olympia, London.

10th–13th June—INSTITUTE OF BRITISH FOUNDRYMEN (Sheffield and District Branch)—Forty-ninth Annual Conference—Buxton.

12th–13th June—SOCIETY OF CHEMICAL INDUSTRY (Chemical Engineering Group)—Conference on Fluidization Technology—Connaught Rooms, Queen Street, Kingsway, Strand, W.C.2.

14th–29th June—DEUTSCHER VERBAND FÜR SCHWEISSTECHNIK—German Welding Association Conference on Welding Technique, and Exhibition—Essen.

18th–20th June—GROUPEMENT POUR L'AVANCEMENT DES MÉTHODES SPECTROGRAPHIQUES—15th Congress of the Organization for the Advancement of Spectrographic Methods—Paris.

24th–28th June—THE INSTITUTE OF PHYSICS—4th Conference on Industrial Physics—"Physics in the Transport, Shipbuilding, and Engineering Industries"—Royal Technical College, Glasgow.

26th June—BRITISH COKE RESEARCH ASSOCIATION—Fifth Conference—"Further Studies of Coking Pressure"—William Beveridge Hall, University of London, Malet Street, W.C.1, 2.30 P.M.

30th June–4th July—ZINC DEVELOPMENT ASSOCIATION—Second International Conference on Galvanizing—Düsseldorf.

TRANSLATION SERVICE

(The previous announcement was made in the May, 1952, issue of the *Journal*, p. 100.)

TRANSLATIONS AVAILABLE

No. 442 (German). E. MARTIN: "Ultrasonic Testing of the Axles of Railway Rolling Stock." (*Stahl und Eisen*, 1952, vol. 72, Feb. 14, pp. 176–185.)

No. 443 (German). H. PANNEK: "Influence of Coil Weight and Roll Speed on the Hourly Output per Stand of Cold Rolling Mills." (*Stahl und Eisen*, 1952, vol. 72, Jan. 17, pp. 70–75.)

No. 444 (German). G. TRÖMEL and W. OELSEN: "Calcium Phosphate Melting Crucibles. On the Metallurgy of the Basic Bessemer Process." (*Archiv für das Eisenhüttenwesen*, 1952, vol. 23, Jan./Feb., pp. 17–20.)

No. 445 (German). W. LUEG: "Rolling Output and Efficiency of Utilization of Cold-Rolling Stands in General Terms." (*Stahl und Eisen*, 1952, vol. 72, Jan. 17, pp. 75–79.)

TRANSLATIONS IN COURSE OF PREPARATION

(German). E. MEIER-CORTÉS: "Experiences with a Box-Type Roof on a 40-Ton Open-Hearth Furnace." (*Stahl und Eisen*, 1952, vol. 72, Jan. 3, pp. 10–12.)

(German). W. LANGE: "Development and Experiences with Basic Chrome–Magnesite Roofs on Large Tilting Open-Hearth Furnaces." (*Stahl und Eisen*, 1952, vol. 72, Mar. 13, pp. 284–287.)

(French). P. ROCQUET and C. G. THIBAUT: "Statistical Study of Some Factors in Relation to the Composition of the Iron from the Blast-Furnace." (*Revue de Métallurgie, Mémoires*, 1951, vol. 48, Apr., pp. 303–313.)

CHARGES FOR COPIES OF TRANSLATIONS—The charge for translations is £1 for the first copy and 10*s*. for each additional copy of the same translation. Requests should be accompanied by a remittance. These translations are not available on loan from the Joint Library.

ABSTRACTS OF CURRENT LITERATURE *and* BOOK NOTICES

IRON AND STEEL MANUFACTURE AND RELATED SUBJECTS

CONTENTS

	PAGE
Mineral Resources	195
Ores—Mining and Treatment	195
Fuel—Preparation, Properties, and Uses	196
Temperature Measurement and Control	196
Refractory Materials	197
Blast-Furnace Practice and Production of Pig Iron	198
Treatment and Use of Slags	198
Direct Processes	198
Production of Steel	198
Foundry Practice	200
Heat-Treatment and Heat-Treatment Furnaces	202
Forging, Stamping, Drawing, and Pressing	202
Rolling-Mill Practice	202
Machinery for Iron and Steel Plant	203
Welding and Flame-Cutting	203
Machining and Machinability	203
Cleaning and Pickling	203
Protective Coatings	204
Properties and Tests	205
Metallography	208
Corrosion	210
Analysis	212
Historical	213
Economics and Statistics	213
Miscellaneous	213
Book Notices	213
New Publications	215

MINERAL RESOURCES

Magnetite-Ilmenite Ores, Their Structure and Degree of Metamorphosis. A. M. Heltzen. (*Tidsskr. Kjemi, Bergvesen Met.*, 1950, **10**, June, 234–237). [In Norwegian]. Some genetic and mineralogical aspects on the chief magnetite ores of Norway are given.—B. S. E.

Sedimentary Iron Ores and Their Transformation. J. A. W. Bugge. (*Tidsskr. Kjemi, Bergvesen Met.*, 1950, **10**, June, 227–234). [In Norwegian]. A presentation is given of some Norwegian iron ores of a magmatic or metasomatic appearance, but which really are transformed sedimentary ores.—B. S. E.

Hematite Deposits at Nussdorf near Unzmarkt. W. Neubauer. (*Berg- hüttenmänn. Monatsh.*, 1951, **96**, Apr., 83–86). A geological survey of the nature and composition of hydrothermal iron-ore deposits in the Mur valley (Austria) is given.

Investigations in the Crystal Chemistry of Silicates. III—The Relation Haematite-Microcline. I. T. Rosenqvist. (*Norsk Geologisk Tidsskrift*, 1951, **29**, 65–76). [In English].

Tungsten and Molybdenum in Sulphide Ores in Northern Sweden. E. Grip. (*Geol. Föreningens Förh.*, 1951, **73**, May–Oct., 455–472). [In English].

The Plane and Linear Structures of the Breitenau Magnesite Deposits. H. Flügel. (*Berg- hüttenmänn Monatsh.*, 1951, **96**, Oct., 205–209).

The Sedimentary Magnesite Deposits in the Palaeozoic of the Western Pyrenees. J. G. de Llarena. (*Berg- hüttenmänn. Monatsh.*, 1951, **96**, Nov., 221–227).

The Geology of the Nickel and Iron Deposits of Lokris in Eastern Greece. W. E. Petraschek, jun. (*Berg- hüttenmänn. Monatsh.*, 1951, **96**, Apr., 76–83).

Observations on the Geology and Mineral Resources of St. Helena. T. Hirst. (*Colonial Geol. Min. Res.*, 1951, **2**, 2, 116–128). The primary object was the investigation of deposits of manganese ore. These were not extensive enough to justify exploitation.—T. E. D.

The Geology and Mineral Resources of (Former) Trans-Jordan. A. M. Quennell. (*Colonial Geol. Min. Res.*, 1951, **2**, 2, 85–115). The overall geology of the area is surveyed. Small deposits of high-grade iron ore, as well as copper and manganese, exist.—T. E. D.

Canada's Iron Ore Resources. J. A. Retty. (*Times Rev. Indust.*, 1952, **6**, Jan., 68–71). The discovery and development of iron ore in New Quebec and Newfoundland-Labrador by the Iron Ore Co. of Canada is traced. A 360-mile railway from Seven Islands, Quebec, to the ore field is under construction. Three deposits are being prepared for open-cast mining. Production is planned to begin in 1954 and is guaranteed a market in the U.S.A. The annual output will be gradually raised to 10 million tons.—H. F.

Trail of '49. (*Metal Market Rev.*, 1951, **4**, Nov. 5, 13–15). The magnitude and importance of the Canadian Ungava iron ore deposits are discussed. Private capital is being used for the development of the mines and the Burnt Creek settlement. Iron content of the ore averages 58·5%, compared with 51·5% for ore from the Mesabi Range in the U.S.A.

T. E. D.

Mineral Exploitation in the United States of Venezuela. J. Luis Barcelo. (*Bol. Min. Indust.*, 1951, **30**, Sept., 413–414). [In Spanish]. Some brief notes on mining activities in Venezuela are given. These cover gold, diamonds, iron ore, coal, copper, bauxite, manganese, asbestos, magnesite, mercury, and graphite.—R. S.

On the Presence of a New Paragenesis of Molybdenite in Seams 7 and 5 of the Bon Azzar Ore Region (South Morocco). G. Jouravsky. (*Compt. Rend.*, 1952, **234**, Jan. 2, 230–231).

ORES—MINING AND TREATMENT

Electrostatic Separation. F. Kvinge. (*Tekn. Ukeblad*, 1951, **98**, Oct. 18, 775–782). [In Norwegian]. The principles of the Johnson and the Sutton electrostatic separators are quoted. Coarse crystalline mixtures of 8–10 mesh grain size are advantageously separated by this method, which can be applied to the Dunderland mixed hematite-magnetite ore.

Agglomeration. (*Chem. Eng.*, 1951, **58**, Oct., 161–174). Methods of agglomeration include pressing, or briquetting, with or without binder, extrusion of plastic masses, tumbling to produce spheres, sintering in stationary and moving hearths, and sintering in rotary kilns.—T. E. D.

Production of Iron Sinter at Helen Mine. K. O. Cockburn. (*Canad. Min. Met. Bull.*, 1951, **44**, Nov., 745–754). By sintering manganiferous siderite, containing 2–3% S, on Dwight-Lloyd machines, a sinter containing 51·8% Fe and 0·066% S is produced, at a rate of 3600 tons/day. The ore, direct from the mine, is crushed to $\frac{5}{16}$ in., and coke 'breeze' from the Algoma Steel Corp. is crushed to $\frac{1}{8}$ in. The sinter mix also includes returned fines from the sinter discharge. Sintering practice is outlined, and details of pelletizing, which is used on very fine materials before sintering, are given.—T. E. D.

XUM

Recent Developments of Band Sintering Plants. H. Wendeborn. (*Stahl u. Eisen*, 1951, **71,** Nov. 8, 1212–1218). The construction of sintering equipment has been improved considerably during the past ten years, particularly in Germany, with respect to driving mechanisms, placing of the sinter cars on, and removing them from, the track rails, and dust removal. The full utilization of existing plants often results in the discharge of red-hot sinter, for the cooling of which new machinery has been developed. The agglomerate is cooled by the passage of air under forced or natural draught. Twin-layer sintering is a technical innovation, in which the lower layer contains approximately one third less fuel than the upper; this saves some 15% of coke. The possibilities of increasing output through lime additions to the ore and the economic limits of draught and layer thickness are discussed. Oxidizing sintering of magnesite ores, first carried out in Sweden, is of special interest.—J. P.

FUEL—PREPARATION, PROPERTIES, AND USES

Combustion Fundamentals. J. Huebler. (*Industr. Heating*, 1951, **18,** July, 1200–1212). In this article the primary forms of the combustion reactions are discussed with particular reference to the types of combustion used in industry. A comparison of the combustion characteristics of different gaseous fuels is made.—J. A. L.

Kinetics of Combustion—Relation to Emission Flame Spectroscopy. K. J. Laidler and K. E. Shuler. (*Indust. Eng. Chem.*, 1951, **43,** Dec., 2758–2761). This is a review of work done on emission flame spectroscopy, and its uses and limitations in the elucidation of combustion processes. Particular attention is paid to the carbon monoxide flame.—C. J. B. F.

Initiation of Detonation in Gases. G. B. Kistiakowsky. (*Indust. Eng. Chem.*, 1951, **43,** Dec., 2794–2797). A qualitative review is made of published facts and theories on the initiation of detonation waves by flames, and the mechanism of propagation of such waves.—C. J. B. F.

International Committee for the Study of Flame Radiation: Comparative Results of Optical Measurements. G. Ribaud, M. Michaud, M. Rivière, and M. J. Galey. (*Chaleur et Ind.*, 1951, **32,** Nov., 301–310). The results of industrial trials are given. Fluctuations in the temperature of emission of the flame were determined by a photoelectric cell in conjunction with a cathode-ray oscillograph; results obtained along the axis of the flame are given in tabular form for all 48 experiments. The contours of the visible part of the flame were measured with a simple cathetometer. The influence of nature and supply of combustible, nature and supply of oxidizing agent, and supply of air of combustion, is reported. The influence of the state of the furnace refractories on the optical measurements was examined and comparisons made between optical measurements and thermocouple readings.

T. E. D.

Predicting the Interchangeability of Fuel Gases. E. R. Weaver. (*Indust. Heating*, 1951, **18,** Oct., 1782–1786). Gases are said to be exactly interchangeable when no difference can be seen or measured in the different flames produced. The author discusses a new method of predicting the extent to which different gases depart from exact interchangeability.

Fuel Economy in the Steel Industry. (*Fuel Econ. Rev.*, 1951, **30,** Dec., 27–34). During the past 30 years, the fuel requirement per ton steel of produced has been approximately halved, the present figure being about 34 cwt./ton steel. Factors affecting the amount of fuel used include the quality of ore, ore preparation, and the properties of the coke. Fuel economies in the melting shop and rolling mill are discussed, and the importance of the integrated plant is emphasized.

A Theory for Turbulent Flow and Its Application to Flow Resistance and Heat Transfer. D. Johnson. (*Tekn. Ukeblad*, 1951, **98,** Sept. 20, 675–681). [In Norwegian]. The author postulates the following formula for the coefficient of friction, ζ, in tubes with a smooth inner surface:

$$\zeta = 0{\cdot}19 \, . \, e^{-\sqrt{\log_e 0{\cdot}00266 \, \mathrm{Re}}}$$

The formula is valid for a range of Reynolds number (Re) from 10,000 to 1,000,000.—B. S. E.

Some Recent Developments in Shallow-Bath Heavy-Media Coal Washing Plant. H. Y. Robinson. (*Min. J.*, 1952, **238,** Feb. 22, 199–201). Attention is drawn particularly to those shallow-bath units using magnetite suspensions. The Vogel Laminarstrom streamline flow washer is described, and is considered an important development, as it is an attempt to extend the range of heavy-media separation down to about 0·75 mm. The Nelson Davis separator, which is likely to become important commercially, is cylindrical; it is described here. The magnetic separator system, used in conjunction with this unit, is also described. Finally, the link-belt concentrator is mentioned.—T. E. D.

Coal Smoke—Its Nature and Prevention. A. C. Monkhouse. (*Chem. Indust.*, 1951, Dec. 22, 1129–1133). The volume and density of coal smoke, arising from the distillation and incomplete combustion of tarry matter in coal and from the mechanical levitation of non-combustible materials, can be measured by suitable techniques either before, during, or after its passage out of a chimney. The methods usually adopted are described.—J. O. L.

Precision of Expansion Tests on Coal—Relation of Expansion to Other Variables. B. W. Naugle, J. D. Davis, and J. E. Wilson. (*Indust. Eng. Chem.*, 1951, **43,** Dec., 2916–2922). Statistics on the reproducibility of both the sole-heated and the large vertical expansion ovens are given in terms of the normal probability law. They include the correlations between expansion and coal particle size as well as wall pressure and internal gas pressure. Formulæ are presented for the estimation of the expansion of coals and certain blends of coals—C. J. B. F.

Expansion Behaviour of Coal during Carbonization. O. P. Brysch and W. E. Ball. (*Gas Times*, 1952, **70,** Feb. 8, 167–175). The physical properties of coals, such as heat of wetting and porosity, are related to volatile matter contents. Expansion pressure, compressibility of charge, coke shrinkage, and the plastic properties of coke during formation are discussed, and an overall mechanism of carbonization is postulated.—T. E. D.

Modern Coking Plants in South Africa. (*Coke Gas*, 1951, **13,** Nov., 377–385). The first modern coking plant in South Africa, complete with by-product recovery and benzole rectification plants, was put into operation in 1934 at the Iscor works at Pretoria. A full description is given of this and four other coke-oven installations, comprising in all 220 W-D Becker ovens, at Pretoria and Vanderbijl Park.—T. E. D.

The Size Grading of Coke for Blast Furnaces. (*Brit. Coke Res. Assoc., Panel No.* 9, First Report, 1951, Aug.). The investigations carried out included the determination and expression of size distribution, and the prediction of degradation during handling. A correlation between blast-furnace performance and coke size was attempted, but the results were inconclusive.—T. E. D.

B.C.U.R.A. Research on Coal Gasification. G. W. C. Allan and S. A. Burke. (*Coke Gas*, 1951, **13,** Dec., 437–438). Field trials on gas-producer practice using a mobile laboratory are outlined, and gasification of coal slurries after 'pelletizing' is mentioned.—T. E. D.

TEMPERATURE MEASUREMENT AND CONTROL

Temperature Measurement and Control. J. L. Garrison. (Amer. Gas Assoc.: *Indust. Heating*, 1951, **18,** Sept., 1562–1572; Dec., 2188–2190). A description of the various temperature-measuring systems and equipment used in gas-fired installations is given. The automatic control systems used to regulate temperatures of gas-burning equipment are also described, and the selection of correct automatic control systems for various gas-heated processes is dealt with.—J. A. L.

High Temperatures in Ferro-Metallurgy, and their Measurement. A. Boitel. (*Mém. Soc. Ing. Civils France*, 1951, **104,** Jan.–Apr., 45–61). The standards used in temperature measurement are the platinum resistance thermometer, −190° to 660° C., the Pt/Pt–Rh thermocouple, 630° to 1063° C., and, above 1063° C., the monochromatic optical pyrometer, based on Wein's formula and the melting point of gold (1063° C.). Practical methods of measurement, and their theory, are outlined, and include thermocouples, monochromatic optical pyrometers, total-radiation pyrometers, and immersion pyrometers.—T. E. D.

Instrumentation for Improved Rolling Temperature Control. L. D. Culp. (*Iron Steel Eng.*, 1951, **28,** Nov., 85–90). This paper discusses the important part that temperature plays in the rolling of high-quality products and describes the instrumentation available for measuring, indicating, and recording these temperatures. Schematic layouts for temperature-measurement installations on hot strip mills and slab heating furnaces are given. The uses of pyrometers for measuring

furnace, moving sheet, rod, rail, and narrow strip temperatures are described.—M. D. J. B.

Temperature Measurements in Wire Drawing with a Wire-Die Thermocouple. W. Lueg. (*Stahl u. Eisen*, 1951, **71**, Oct. 25, 1140–1145). Drawing tests have been carried out on a patented steel wire and a low-carbon wire rod under various working conditions, and the temperature in the die measured continuously with a thermocouple formed from the carbide die and the wire being drawn. The results show that the wire-die thermocouple is suitable for indicating the temperature conditions during drawing—J. P.

Studies of Slags and Inclusions. G. P. Chatterjee, S. Pramanik, and G. Mukherjee. (*Metal Market Rev.*, 1951, **4**, Nov. 5, 13–15). A simple laboratory micropyrometer is described for use in the study of melting points or melting ranges of slags and inclusions and some surface characteristics at elevated temperatures. The micro-sample, which is viewed through a microscope, is heated electrically on a thin platinium foil, to which is welded the hot junction of a Pt/Pt–Rh thermocouple. Samples were heated up to temperatures of 1500° C.—T. E. D.

REFRACTORY MATERIALS

The Behaviour of Firebricks on Reheating. Part II. After-Contraction and After-Expansion under Reducing Conditions. F. H. Clews, J. F. Clements, and A. T. Green. (*Trans. Brit. Cer. Soc.*, 1951, **50**, Oct., 415–423). The effects of furnace atmospheres on the behaviour of firebricks at 1400° C. have been studied. One set of tests was carried out in an atmosphere containing 9·4% CO_2, 4·6% O_2 during heating, and 9·7% CO_2, 4·1% O_2 during the soaking period; and a second set in an atmosphere containing 8·0% CO_2, 0·0% O_2, 5·0% CO, heating period, and 7·2% CO_2, 0·0% O_2, 6·4% CO, soaking period. Under the latter conditions, defined as reducing, a greater contraction or a smaller expansion resulted than would have occurred under the oxidizing conditions reserved for the first set of tests.—E. J. D. S.

The Behaviour of Firebricks on Reheating. Part III. Some Possible Modifications in the Reheat Test. F. H. Clews, J. F. Clements, and A. T. Green. (*Trans. Brit. Cer. Soc.*, 1951, **50**, Oct., 424–431). Expansions could be prevented in the reheat test by applying a small load to the specimen, but it was impossible to choose a load that would check every expansion without causing excessive deformation in some materials. A double test in which duplicate specimens are reheated at 1400° and 1250° C. respectively, allowing only a nominal length change at the lower temperature while retaining the present limits at 1400° C., is suggested as an alternative to the present test.—E. J. D. S.

The Behaviour of Firebricks on Reheating. Part IV. Variability of Reheat Behaviour in Firebricks. J. F. Clements and G. R. Rigby. (*Trans. Brit. Cer. Soc.*, 1951, **50**, Oct., 432–444). Many after-contraction tests were carried out on 19 brands of firebrick. A fairly accurate average value could be obtained from a small number of tests on some brands, but on others 20 tests or more were necessary to ensure that the mean value of the results was sufficiently near the true value for the batch. The estimation of the number of tests required by calculating the standard deviation, and the errors involved, are discussed. Analysis of the variation in reheat behaviour within single bricks, between one brick and another within a batch, and in different directions in the same test piece suggests that all three types of variation should be considered when sampling.—E. J. D. S.

The Behaviour of Firebricks on Reheating. Part V. Some Observations on the Causes of After-Expansion in Firebricks. J. F. Clements and G. R. Rigby. (*Trans. Brit. Cer. Soc.*, 1951, **50**, Oct., 445–459). Three possible causes of after-contraction in firebricks are discussed : (*a*) Bloating, (*b*) laminar splitting or exfoliation, and (*c*) expansion of the solid material. An attempt to relate the after-expansion to some of the physical and chemical properties of these bricks is described. Experiments on an exfoliating clay are also described. Another substance, such as sulphur, in addition to ferric oxide and carbon, may contribute to the behaviour of firebricks on reheating.—E. J. D. S.

X-Ray Investigation of Calcium Orthosilicate Ca_2SiO_4 at Temperatures up to 1500° C. G. Troemel and H. Moeller. (*Silicates Indust.*, 1951, **16**, Nov., 300–301). [In English]. By X-ray diffraction measurements at high temperatures the existence has been confirmed of two new high-temperature modifications predicted by M. A. Bredig on the basis of crystal-chemical considerations. Above about 1450° C. there is a stable hexagonal α-phase, between 675° and 1450° C. an orthorhombic α′-phase. The investigation on the low-temperature β- and γ-phases is not yet completed. On heating, both these phases are transformed to the α′-phase. The γ-phase is stable far above 675° C.—P. F.

A Quantitative X-Ray Crystallographic Method of Analysing Polymorphic Transformations of Silica. W. L. De Keyser. (*Silicates Indust.*, 1951, **16**, Nov., 296–299). A method, based upon the use of an X-ray spectrometer employing a Geiger counter, used for estimating the amount of quartz, tridymite, and cristobalite in silica bricks is described. It is quantitative, and superior to both density and dilatometric methods.—P. F.

Microscopic Observations on Silica Bricks. C. Schouten. (*Trans. Brit. Cer. Soc.*, 1951, **50**, May, 185–207). Some of the mineralogical changes that take place when raw silica bricks are fired for 24 hr. at various temperatures up to 1480° C. are described. The effects of adding small amounts of various minerals to the bricks and exposing them to furnace conditions are briefly discussed. Mineralogical changes in open-hearth silica bricks during service are also described and explanations are offered.—E. J. D. S.

Comparative Tests on the Suitability of Two Refractories for Pouring Runners. G. Ziliani and G. Grungo. (*Met. Ital.*, 1951, **43**, Nov., 476–481). The presence of free quartz causes poor resistance of refractories to the chemical action of molten steel. If the steel has a normal manganese content fairly good results can be obtained even with low alumina refractories. The authors investigated two of these refractories, of almost identical composition. The difference in their behaviour is due to the quantity of flux, the free quartz, perhaps to the development of mullite before the melting of the refractory, and lastly to the tribometric resistance of the materials.—M. D. J. B.

Differential Thermal Analysis of Clay Minerals under Controlled Thermodynamic Conditions. R. L. Stone. (Ohio State University Studies, 1951, Engineering Experiment Station Bulletin No. 146).

Applications of the CaO–Al_2O_3–SiO_2 Ternary System to Brick–Slag Reactions. W. F. Ford and J. White. (*Trans. Brit. Cer. Soc.*, 1951, **50**, Nov., 461–505). The metallurgical technique of constructing vertical sections through ternary equilibrium diagrams was applied to the CaO–Al_2O_3–SiO_2 system to show the melting and phase relations of mixtures of refractory brick and blast-furnace slag. This information could be correlated with the results of practical slag tests in which equilibrium conditions were approximated. The amount and viscosity of the ternary eutectic liquid formed was the major factor influencing softening behaviour.

Basic Refractories and Slags for Electric Steel Furnaces. A. H. Thomson. (*Amer. Foundryman*, 1951, **20**, Sept., 52–54). The properties, service conditions, and applications of basic refractory linings and patching materials for electric furnaces are considered and discussed.—E. J. D. S.

British Report on All-Basic Openhearths. M. Davies. (*Iron Age*, 1951, **168**, Oct. 4, 225–228). Comparative figures of five campaigns of all-basic furnaces in the United Kingdom and Holland are given. The advantages indicated include increased output, reduced man-hours for bricklaying, less slag bulk, reduction in shutdown time, and most advantageous use of liquid fuels. Built-in roof pressure indicators are helping with design and construction.—A. M. F.

Refractory Linings for Open-Hearth Furnaces : A Comparison between Acid and Basic Linings. A. Scortecci and F. Savioli. (*Met. Ital.*, 1951, **43**, Dec., 521–525). The authors have studied three types of lining for open-hearth furnaces : (1) The traditional silica brick lining, with or without basic bricks in certain parts. (2) The raw quartzite packed lining, now used for all parts of the furnace, except the roof ; with this, front, back, and end-wal repairs are possible while the furnace is in operation. This process was first developed in Italy. (3) The all-basic lining in magnesite and chrome-magnesite bricks. This lining has been developed and improved by full-scale trials. The authors conclude that were it not for the swelling of chrome-magnesite bricks, the all-basic furnace would have unquestionable advantages over all other types.—M. D. J. B.

Bottom Building and Maintenance. H. C. Bigge. (*Amer. Inst. Min. Met. Eng., Proc. Elec. Furn. Steel Conf.*, 1950, **8**, 49–69). The author discusses the problem of correct bottom building and maintenance in basic electric furnace practice. After a general discussion three modern methods of bottom ramming are described, which involve the use, respectively, of a periclase–magnesite mixture, magnesia refractory, and a new material containing about 96% MgO. The installation of new brickwork and rammed bottoms in 25-ton and 50-ton furnaces at Bethlehem Steel Co. is then described in detail.—G. F.

Types of Roof Construction. T. A. Blackwell. (*Amer. Inst. Min. Met. Eng., Proc. Elec. Furn. Steel Conf.*, 1950, **8**, 72–75). The author describes the basic electric furnace roof construction in current use at Atlas Steels Ltd., Welland, Ontario. Details are given of trials of mullite roofs at this works, which showed that the increased life obtained, as compared with silica roofs, was not sufficient to outweigh the extra cost. Trials which are planned with super-duty silica brick and rammed monolithic roofs are also briefly outlined.—G. F.

High Temperature Insulating Materials, Their Properties and Testing. J. F. Clements. (*Inst. Gas Eng., Proc. Conf. on Heat Insulation*, Nov. 30, 1950, 92–122). The thermal, mechanical, and refractory properties required in high-temperature insulating materials are summarized and methods of measuring refractory properties are discussed. Hot-face insulation is compared with backing-up insulation. The applicability of various methods of measuring thermal conductivity, bulk density and porosity, and permeability is appraised. To give results reproducible within 1%, thermal conductivity apparatus must have: (1) A heating system which is sufficiently flexible to heat the face of the test panel uniformly; (2) an automatically controlled temperature; (3) a calorimeter system designed so that the calculated conductivity value is independent of the rate at which water is flowing in the calorimeter; and (4) an independent water supply drawn from a constant-head tank. The properties of insulating bricks are tabulated.—E. C. S.

Silicon Carbide Refractories Used as Alternates for Special Service Alloys. J. L. Everhart. (*Mat. Methods*, 1951, **34**, Nov., 71–75). Bonded silicon carbide gives a combination of good elevated temperature properties, and high abrasion and corrosion resistance. It is therefore being used in ever increasing quantities where strategic alloy steels were previously necessary. Its properties are discussed.—P. M. C.

Heat Losses of Insulated Pipes. U. Grigull. (*BWK*, 1951, **3**, Aug., 253–258). [In German]. A method is described for direct determination of heat losses, without estimation or calculation of the surface temperature of the insulation. Two nomograms for graphical solution are included. The method may also be used for solution of other problems, *e.g.*, maintenance of an accepted heat loss or of a given surface temperature.—E. C.

BLAST-FURNACE PRACTICE AND PRODUCTION OF PIG IRON

Related Diffusion Effects of Carbon and Sulphur in Iron at High Temperatures. K. J. Irvine. (*J. Iron Steel Inst.*, 1952, **171**, June, 142–147). [This issue].

Action of Inhibitors of Carbon Deposition in Iron Ore Reduction. S. Klemantaski. (*J. Iron Steel Inst.*, 1952, **171**, 176–182). [This issue].

TREATMENT AND USE OF SLAGS

Some Investigations of Reactions between Iron and Cobalt with Basic Slag in the Solid Phase. I. T. Rosenqvist and G. Taralrud. (*Tidsskr. Kjemi, Bergvesen Met.*, 1950, **10**, Jan., 7–8). [In Norwegian]. The reaction rate for metal/basic slag [$Ca_3(PO_4)_2$] is faster in nitrogen atmosphere than in argon. The kinetics of these reactions are much accelerated in hydrogen, which is not surprising as the hydrogen is continuously reducing the metal oxides as in the Redox process.—B. S. E.

Activation of the Process of Hardening of Slag Cements. P. P. Budnikov, V. N. Yung, and Yu. M. Butt. (*Doklady Akademii Nauk S.S.S.R.*, 1951, **79**, 851–854). [In Russian]. Finely ground granulated blast-furnace slags possess either very weak or no bonding properties. To induce reaction of slag with water, alkaline or sulphate activators are necessary. Burned lime and gypsum were used as activators with satisfactory results. MnO in slag has a deleterious effect on bonding properties of cement and therefore the slag should not contain more than 1·5–4·0%. Hydration properties of slags are considerably improved by wet grinding in a ball mill. When wet grinding is done with about 5–10% of lime the cement obtained is stronger than when 30% of portland cement clinker is added and dry grinding is used.—V. G.

Some Observations Relating to The Use of Slag In Cement Production. G. Batta and R. Plenger. (*Silicates Indust.*, 1952, **17**, Jan., 11–14). Work done by the authors and others on the constitution, strength, and resistance to attack by saline solutions of self-setting, slag-bearing cements is reviewed, and the economical aspects, particularly reduced lime requirements in slag cements, are discussed. Disintegration of slag-bearing cements in a solution containing 20 g. $MgSO_4$ per litre of water was found to be preceded by swelling, which did not occur if disintegration took place in sea water. Magnesium sulphate solutions are thus unsuitable as rapid indicators of the resistance of the cements to attack by salt water.—P. F.

DIRECT PROCESSES

Controlled Density Steel. (*Engineer*, 1951, **192**, Dec. 28, 839–840; *Steel*, 1951, **129**, Dec. 10, 123); *Canad. Metals*, 1952, **15**, Jan., 17–18). An account is given of a process developed by the Ontario Research Foundation for producing finished and semi-finished articles of steel having any desired density and analysis within a very wide range. Briefly, fine ore is made directly into the desired steel shape by reduction at about 2000° F. in the mould. The resulting article has the composition and structure of normal steel but contains a predetermined number of spherical voids. Whilst the density of steel is about 7·8 g./c.c., controlled density steel can be produced with any desired density from 1·0 to 7·2 directly from the furnace.—M. D. J. B.

PRODUCTION OF STEEL

Colombia's Integrated Steelworks. (*Times Rev. Indust.*, 1952, **6**, Jan., 83–84). A small integrated steelworks is under construction at Paz del Río, in the Andes, which is close to large supplies of iron ore, coal, and limestone. The plant is to go into operation in July 1953. It includes one blast-furnace (500 tons of pig iron per day), a coke plant with 43 ovens, and a steel plant with three converters of 22 tons each. The ultimate annual capacity is 122,000 tons of all types of rolled and drawn steel.—H. F.

J. & L. Pours First Steel from New Melt Shop. (*Iron Steel Eng.*, 1951, **28**, Nov., 122–126). A description is given of the new Pittsburgh plant of Jones and Laughlin Steel Corp. The expansion includes the construction of 11 new open-hearth furnaces with an annual capacity of 2,000,000 tons. Features of the new plant include latest developments in open-hearth furnace design, instrumentation for high-efficiency temperature control, efficiency of fuel utilization, mechanized material handling facilities, provisions for using tar, oil, or gas for fuel, and special scrap-handling facilities.—M. D. J. B.

The Iron and Steel Works of Nazionale Cogne S.p.A.: Production of Special Steels, Steel Tubes and Sheet. (*Iron Coal Trades Rev.*, 1951, **163**, Dec. 28, 1411–1413). In this summary of the activities of the Nazionale Cogne S.p.A., which forms an important part of the Italian iron and steel industry and engineering industry, brief descriptions are given of the Cogne and Aosta iron and steel works, the Imola engineering shops, and the Castellamonte refractories department. The steelworks produce a range of high-grade and special steels, including high-speed and stainless steels, and also steel tubes and sheet.—G. F.

The Völklingen Forges and Steelworks. (*Mét. Constr. Mécan.*, 1951, **83**, Nov., 940–942). The capacity of the Völklingen works is 800,000 tons/annum, of which 165,000 tons are special steels. The works comprise six blast-furnaces; five converters; coke ovens; blooming, section, joist, and rail mills; and wire rod and strip mills. The special steel department has three 60-ton open-hearth and five electric furnaces.—R. S.

Quality Control and Problems of Choice of Grade for Ordinary and Special Quality Steels. H. Hoff. (*Stahl u. Eisen*, 1951, **71**, Nov. 22, 1293–1304). The supervision of materials

and quality in an integrated steelworks is illustrated with reference to three examples: the production of a rimmed and a killed open-hearth steel for deep drawing, and of a rimmed Bessemer free-cutting steel. In addition to the usual chemical and mechanical testing of the steel and the materials used in melting, a statistical examination of all the production conditions during teaming, solidification, and rolling is necessary. This offers, in conjunction with the other tests, the possibility of recognizing and eliminating sources of defects such as segregations, internal and external flaws, and of predicting the properties of a heat and thus avoiding incorrect processing. Conclusions can thus be drawn as to the appropriate use of the heat, the necessity of scarfing the ingots, and the correct cropping of top and bottom. The results of this statistical evaluation are given. In a mixed steelworks there easily arises a multiplicity of grades, which is an advantage to the consumer. The number of grades should be kept to a minimum on grounds of easier stocking and economic production, and should be restricted to standard steels.—J. P.

Hydrodynamic Study of Air Movements in the Bath of a Basic Bessemer Converter. G. Husson. (*Rev. Univ. Min.*, 1951, Series 9, **7,** Dec., 436–439). A description is given of tests carried out on small-scale models and a full-size converter. The difficulty of scaling down the size and the fluid in order to obtain similarity with full scale is reported. Scale models of 1/100, 1/10, 1/7·5 and 1/5·2 full size have been constructed. Effects observable on the full-size converter can be accurately reproduced on the models. Suggested modifications in converter design will be reported elsewhere.—B. G. B.

The Use of Oxygen/Carbon-Dioxide instead of Air in the Final Stage of the Basic Bessemer Process. B. Kalling, F. Johansson, and L. Lindskog. (*Jernkontorets Ann.*, 1951, **135,** 10, 557–572). [In Swedish]. The use of 1 : 1 O_2–CO_2 mixtures for blowing a 14-ton converter has reduced the nitrogen in the steel from 0·012%, obtained with air-blowing, to 0·006%.—B. S. E.

Metallurgy and Economics of Oxygen Enrichment in Air-Refining. R. Graef. (*Stahl u. Eisen*, 1951, **71,** Nov. 8, 1189–1198). It has been shown that the nitrogen content of basic Bessemer steel can be reduced from the usual 0·016% to 0·005–0·006% by the use of oxygen-enriched air and ore additions. The phosphorus content also is lowered from 0·055% to 0·035%. Further advantages of the use of oxygen are reduced blowing time, the possibility of using a low-phosphorus charge and larger quantities of iron ore, and improved life of the converter lining. Disadvantages are increased amount of iron in, and reduced citric acid solubility of, the slag. Refining of pig iron, pre-blown with oxygen-enriched air, further reduces the nitrogen content by 0·001–0·002%, and such pre-blown iron can be refined with air alone to give low-nitrogen steel. This pre-refined iron is easily blown; 35 tons could be worked in a 20-ton furnace without loss. Trials have shown that, with more oxygen in the air, the nitrogen content can be reduced in practice to under 0·004% in the steel, and that the oxygen concentration need not exceed 40–45% to do this. The slag resulting from the pre-refining is a suitable raw material for the recovery of vanadium and manganese. The economic position of this method of refining is assured.—J. P.

Flow Patterns in Furnaces. J. H. Chesters. (*Coke Gas*, 1951, **13,** Nov., 391–394). A brief account is given of the work of The United Steel Companies, Ltd., on the flow of gases in furnaces. As a preliminary study, flow in two dimensions was examined. This was followed by work on three-dimensional geometrical systems, on hot models, and on full-size furnaces. Whether or not flow in furnaces should be streamlined is discussed.—T. E. D.

Experiences with a Box-Type Roof on a 40-Ton Open-Hearth Furnace. E. Meier-Cortés. (*Stahl u. Eisen*, 1952, **72,** Jan. 3, 10–12). The use of a box-type roof has advantages even for an open-hearth furnace with good roof performance. The longer life renders possible a higher steel production as well as better furnace utilization. The economics of the melting operation can be further improved, with furnaces with sufficiently large slag pockets, if the usual renovation after 500–600 heats is dispensed with.—J. P.

Port Ends of Open-Hearth Furnaces Fired with Coke-Oven Gas. F. Wesemann and W. Schmitt. (*Stahl u. Eisen*, 1951, **71,** Dec. 20, 1413–1420). Designs of port ends and operating data from 22 cold-gas-fired furnaces have been evaluated. Dividing the furnaces into high, medium, and low output groups provided a basis for assessing port design. The results emphasized the importance of number of gas jets, gas velocity, air velocity in the uptakes, height of the nose of the jet above bath level, length of premixing chamber, gas jet angle, and the steepness of the ramp and its roof. It was then possible to make recommendations as to the best port design. These results can be extended if each works keeps a record of any changes in port design and resulting operating figures over several campaigns.—J. P.

The Effect of Sodium Oxide Additions to Steelmaking Slags: Pt. II—Dephosphorization of Steel by Soda Slags. W. R. Maddocks and E. T. Turkdogan. (*J. Iron Steel Inst.*, 1952, **171,** June, 128–136). [This issue].

Copper Contamination in Open-Hearth Steel. G. Rockrohr. (*Stahl u. Eisen*, 1952, **72,** Jan. 31, 118–122). Works' data indicate that the copper content of open-hearth steel has increased from a mean value of 0·15% in 1923 to 0·23% after the war. The improvement noticeable in 1950 is attributable to the increased price for scrap copper alloys and thus the better sorting of steel scrap. It has been shown that a considerable proportion of the copper contamination arises from copper and brass mixed with bought scrap; other sources are mentioned. The deleterious effects of copper in steel are discussed and the requirements of the steel fabricator for low sulphur materials are contrasted with the possibilities open to the producer. It is shown how, in the long run, the copper content of steel can be controlled within tolerable limits, and a method is described for the rapid estimation of copper in steel.—J. P.

Shortening the Heating-Up Time of Open-Hearth Furnaces. (*Hutnické Listy*, 1951, **6,** Feb., 85). [In Czech]. Experiments were made at the Třinec steelworks to shorten the heating-up time of open-hearth furnaces after repairs. Originally 96 to 108 hr. were necessary. This was reduced to 54 hr. in one furnace, and the heating schedule applied is described.—E. G.

Technique for Radiochemical Investigations of Metallurgical Processes. Study of a 50-ton Open-Hearth Furnace. W. Koch and K. Fink. (*Arch. Eisenhüttenwesen*, 1951, **22,** Nov.–Dec., 371–375). It has been shown, by injecting radioactive sulphur S^{35}, in the form of dilute sulphuric acid, into the gas uptake of a 50-ton open-hearth furnace, that even with a charge of light scrap, the sulphur pick-up from the gas was small compared with the sulphur introduced in the charge. With a mean sulphur content in the gas of 54 g./100 cu. m. and a final sulphur content of 0·016% in the steel and 0·30% in the slag, 11–12% of the sulphur in the steel and slag came from the gas phase. Sulphur pick-up from the gas occurred almost exclusively during melting down. During the boil, a constant interchange of sulphur took place between the gas and slag. Only when the carbon drop reached a high value was there also an interchange of sulphur between the metal and slag.—J. P.

The Thermodynamics of Substances of Interest in Iron and Steel Making: III—Sulphides. F. D. Richardson and J. H. E. Jeffes. (*J. Iron Steel Inst.*, 1952, **171,** June, 165–175). [This issue].

Addition of Boron to Steel by Reduction from Boron Oxide. G. E. Speight. (*J. Iron Steel Inst.*, 1952, **171,** June, 147–153). [This issue].

Sub-Surface Ingot Structure of Semi-Killed Steel. R. Wogin and A. Goodall. (*J. Iron Steel Inst.*, 1952, **171,** June, 154–159). [This issue].

Some Methods of Increasing the Life of Open-Hearth Furnaces. P. P. Budnikov, D. P. Bogacky, A. A. Lebedkov, and J. L. Rozenblit. (*Izvest. Akad. Nauk S.S.S.R., Otdelenie tekhnicheskikh Nauk*, 1950, No. 6, 901–912; *Hutnické Listy*, 1951, **6,** June, 300–304). [In Czech]. In this report on the life of open-hearth furnace linings and roofs in Russian steelworks it is suggested that two or more burners would give more uniform wear by reducing turbulence. The authors believe that a real improvement in life can be obtained only by substituting basic refractories for the acid Dinas in places subjected to high stress and wear.—E. G.

The Specific Electrical Conductance of Aqueous Extracts of Slags as a Means of Determining Basicity. W. A. Fischer and H. v. Ende. (*Stahl u. Eisen*, 1952, **72,** Jan. 31, 146–147). The work of W. A. Smith, J. Monaghan, and W. Hay (*J. Iron Steel Inst.*, 1948, **160,** Oct., 121–130) has been repeated on 90 samples of open-hearth slags. The general conclusions of these authors that log (conductance) is a linear function of

log [CaO/(SiO_2 + P_2O_5)] are confirmed, but the errors (± 0·3 in the value of basicity for a given conductance), in spite of great care in carrying out the test, are too great for the method to be considered suitable for slag control.—J. P.

FOUNDRY PRACTICE

Basic-Lined Water-Cooled Cupola at Lynchburg Foundry. W. W. Levi. (*Foundry Trade J.*, 1952, **92,** Jan. 10, 45–48). The basic-lined cupola described was built to provide grey iron with the graphite in nodular form and to produce iron for spun pipe. Iron for this pipe can be produced in the basic cupola with charges containing 50–70% steel scrap and little or no pig iron.—R. A. R.

Operation of Hot-Blast Cupolas. F. C. Evans. (*Foundry Trade J.*, 1951, **91,** Aug. 30, 247–251; Sept. 6, 279–282). This paper summarizes the advantages of the hot-blast cupola process, which is much more common on the Continent than in Britain, and deals with the solutions to the engineering problems that it involves. The advantages are less coke consumption, use of the low-grade coke, increased output of melted iron, lower loss of manganese and silicon, increased carburization and decreased sulphur, and hotter iron, which is less oxidized. The problems include the choice of refractory, the reduction of recuperator efficiency by dust, and heat losses.—E. T. L.

Basic Cupola Melting and Its Possibilities. E. S. Renshaw. (*Foundry Trade J.*, 1951, **91,** Aug. 23, 205–210). The characteristics of a typical cupola, and its action in removing sulphur and silicon, are discussed. The author considers increasing the carbon pick-up, and the effect of the slag composition, choice of refractories, and water cooling. The main point is the consideration of basic operation.—E. T. L.

New Mechanised Cupola Charging System. (*Foundry Trade J.*, 1951, **91,** Nov. 1, 495–498). This is a description of the melting unit at the works of the International Harvester Co. Particular attention is given to a novel swivel-hoist charger for the cupolas, which replaces both the usual transfer car and charging crane.—E. T. L.

Mechanical Charging of Cupolas. W. J. Driscoll. (*Inst. Brit. Found.*, 1951, June 12–15, Preprint No. 1009: *Found. Trade J.*, 1951, **91,** Nov. 15, 551–560; Nov. 22, 597–605; Nov. 29, 629–637). This review of existing methods, especially those in America, mentions the advantages of mechanical charging, and various types of skip, hoist, and charger. The charging of coke and limestone receives particular attention. The author considers stockyard arrangement, bulk density of common materials, and labour requirements.—E. T. L.

Quantity Production of Spheroidal-Graphite Cast Iron. N. Croft. (Brussels International Foundry Congress: *Foundry Trade J.*, 1952, **92,** Jan. 3, 5–11). Adding magnesium to molten cast iron produces spheroidal cast iron. The author describes how this is done on a commercial scale, pointing out that a self-contained section of the foundry should be provided for the exclusive production of this material. E. T. L.

Rôle of the Metallurgical Department in Works Control. V. W. Childs. (Inst Brit. Foundrymen: *Foundry Trade J.*, 1951, **91,** Dec. 27, 735–736). The metallurgical department should control all purchased metals, moulding materials, fuels and fluxes, and processes, particularly melting and heat-treatment.—R. A. R.

Gaseous Annealing of Malleable Castings. J. C. Mantell, (*Foundry Trade J.*, 1951, **91,** Dec. 27, 741–744). The author summarizes experience with a Birlec 300-kW. electric malleablizing furnace. He describes the packing of the castings, and discusses the improved surface finish and freedom from warping, and the cost of electricity, labour, and maintenance. E. T. L.

Evaluation of Soundness in Cast Iron. (*Foundry Trade J.*, 1951, **91,** Aug. 23, 211–219; Aug. 30, 253–260; Sept. 6, 283–291). This is a report of sub-committee T.S.20 of the Inst. Brit. Foundrymen Technical Council. The committee had to examine and recommend methods of evaluating soundness in cast iron with a view to using such methods in subsequent investigations on the effect of mould materials on grey and malleable iron castings. The first section deals with radiographic methods, and the second with ultrasonic flaw detection and electrical and magnetic methods. The final section is about density determinations, pressure testing, and other methods.—E. T. L.

Symposium on Vermiculite in the Foundry. J. E. Laschinger, G. Butler, A. Hirst, and B. Haigh. (Inst. Brit. Foundrymen: *Foundry Trade J.*, 1952, **92,** Jan. 24, 89–92). The first author describes the composition and uses of vermiculite, and the second outlines the application to castings; A. Hirst recommends its use in steel casting, and B. Haigh lists recently discovered fields of application.—E. T. L.

Measurement of Plastic Flow in Moulding Sands. A. Jamieson. (*Foundry Trade J.*, 1951, **91,** Sept. 6, 271–277). Plastic flow is defined as flow where the grains remain partially bound together, and is measured by a modification of the Buchanan compression tester, in which deformation under compression is measured against load. Results are given for the effect of moisture content and time of milling.—E. T. L.

Production Aids in The Steel Foundry. G. D. McNair. (Inst. Brit. Foundrymen: *Foundry Trade J.*, 1952, **92,** Jan. 24, 83–86). This paper describes the advantages found in practice, using the knock-off or Washburn core technique in moulding. Details are given of the process and of typical applications.—E. T. L.

Briquetting of Cast Iron Turnings. A. M. Bielawski and M. J. Korniuszin. (*Liteinoje Proizvodstvo*, 1951, No. 4; *Przeglad Odlewnictwa*, 1951, **1,** Nov. 324–325). [In Polish]. Briquetting of cast-iron turnings and their melting in a cupola are described.—V. G.

Malleable Cast Iron—Annealing Furnaces and Atmosphere. O. E. Cullen and R. J. Light. (*Trans. Amer. Found. Soc.*, 1951, **59,** 484–500). The construction and operation of a modern controlled-atmosphere continuous malleablizing furnace is described. The problems attending its use are mentioned. A description is also given of various types of atmosphere, and their control.—P. C. P.

Simplifying the Moulding For Medium-Size Castings. A. Cappon. (*Metalen*, 1951, **6,** Dec. 15, 441–447). [In Dutch]. Considerable economy is effected in moulding time, pouring time, mould materials, and transport if what the author terms the 'moulding with joint facing upward' method is used. Cement sand can be used instead of loam in this semi-permanent mould system.—R. S.

Practical Hints on Core Blowing. W. Chabowski. (*Przeglad Odlewnictwa*, 1951, **1,** Dec., 335–339). [In Polish]. General principles of core blowing are discussed and practical hints on core preparation by this method are given.—V. G.

Strickled-Top Coreboxes. (*Foundry Trade J.*, 1952, **92,** Jan. 31, 125). This brief note proposes the use of core boxes in which a shaped top surface of the core is obtained by scraping a flat edge between two opposite similarly shaped sides of the box. This type of box is cheaper to make than the more usual box in which the shaped surface is cut from the solid in the base of the box.—E. T. L.

The Timed Jolt. H. J. Bullock. (*Foundry Trade J.*, 1951, **91,** Aug. 2, 125–127). Moulding machines can be improved by greater control of the number and amplitude of the vibrations the mould suffers. Photographs show the effect of using different numbers of jolt.—E. T. L.

Castings for the Corliss Steam Engine. D. Redfern. (*Foundry Trade J.*, 1951, **91,** Aug. 9, 157–162, 164; Aug. 23, 221–225). Illustrations and text describe the making of a large flywheel, a trunk guide soleplate, and a cylinder.—E. T. L.

Application of Time-Study to Moulding Operations. G. Martin. (*Foundry Trade J.*, 1951, **91,** Aug. 30, 261–262). The times taken for typical founding processes are given, and the author outlines the value of such measurements in practice, for piece work, progressing of orders, and planning of layout.—E. T. L.

Casting Drop-Hammer Dies. (*Aircraft Prod.*, 1952, **14,** Feb., 59–64). The use of expanding plasters for the production of close-tolerance patterns is described, and the water-to-gypsum ratios for various degrees of expansion are listed. T. E. D.

Precision Casting of Heat-Resistant Alloys at Allis-Chalmers. (*Indust. Heating*, 1951, **18,** Oct., 1810–1822, 1915, 1916). A new plant at Allis Chalmers Manufacturing Co., Milwaukee, for precision casting by the 'lost wax' process is described. Typical parts cast are gas-turbine blades and stator discs with integrally cast blades.—J. A. L.

Shell Molding—Advantages are Numerous. B. M. Ames. (Malleable Founders Society: *Steel*, 1951, **129,** Dec. 3, 90–92). The techniques of shell moulding are discussed. The process, in which the thermosetting properties of phenolic resins are

utilized to provide a bond material for silica grains in the construction of the mould, can give production economies when applied to the right job. Quantity production is required and the casting must lend itself to suitable heading and gating arrangements. Another important factor is the amount of cleaning and machining that can be saved.—A. M. F.

Precision Casting Process. W. H. Sulzer. (*Foundry Trade J.*, 1951, **91,** Dec. 20, 699–707). This is an English translation of a paper which appeared in *Neue Giesserei*, 1950, **37,** Dec. 14, 557–565. (*See J. Iron Steel Inst.*, 1951, **169,** Oct., 189).

Precision Founding by the Lost Wax Process and Its Applications to the Pouring of Small Mechanical Castings. E. Morlet. (*Usine Nouvelle*, 1952, **8,** Jan. 10, 27). The lost-wax process is described.—T. E. D.

The Manufacture of Sheets Directly from Liquid Iron. E. G. Nikolajenko. (*Selkhozmashina*, 1951, No. 4 : *Przeglad Odlewnictwa*, 1951, **1,** Dec., 340–341). [In Polish]. A process of producing sheet iron directly from liquid iron is described. The process consists of melting the metal in a cupola, formation of sheets by teeming on to water-cooled rolls, suitable heat-treatment, and finishing to obtain sheets of required size. The chemical composition of the metal was similar to grey iron with silicon up to 2·2% and phosphorus from 0·15 to 0·20%. Russian factories are at present producing by this method iron sheets 0·5 to 1·2 mm. thick, 500 mm. wide, and 750–1000 mm. long. The structure and the mechanical properties of the sheets are described. These can be modified according to requirements by the chemical composition of the metal and heat-treatment (graphitizing or decarburizing). The cost of cast iron sheets is 25–50% cheaper than steel sheets and in addition they are 8–9 times more resistant to corrosion.—V. G.

A Foundry for an Oil Engine Works. (*Engineer*, 1951, **192,** Dec. 21, 811–812). **Crossley Brothers Modern Foundry Developments.** (*Foundry Trade J.*, 1952, **92,** Jan. 10, 31–36 ; *Oil Engine and Gas Turbine*, 1952, **19,** Jan., 362–363). This article describes the new foundry built to produce a wide variety of castings both for Crossley Brothers Ltd. and for its associate firm, Crossley Premier Engines Ltd.—M. D. J. B.

Castings for a Small Diesel Engine. H. J. M. Conacher and R. Leeks. Inst. Brit. Foundrymen : *Foundry Trade J.*, 1952, **92,** Jan. 17, 57–65). This is a well-illustrated description of the manufacture of diesel-engine castings by Alexander Shanks and Son, Ltd.—E. T. L.

Carron Mechanized Bath Foundry. B. McCall. (Carron Cupola : *Foundry Trade J.*, 1951, **91,** Dec. 20, 709–711). The author briefly describes the layout, preparation of moulds, and dressing of castings at the works of the Carron Company, Carron, Scotland.—E. T. L.

Ferranti Foundry : Innovations in Mechanized Production. V. C. Faulkner. (*Foundry Trade J.*, 1952, **92** ; Feb. 7, 139–144 ; Feb. 14, 165–168). This is a detailed description of the layout and equipment at the Hollinwood works of Ferranti Ltd., which specializes in the production of a high nickel, non-magnetic alloy.—E. T. L.

Production of Heavy Castings for Electrical Generating Equipment. N. Charlton. (*Inst. Brit. Found.*, 1951, June 12–15, Preprint No. 1001 : *Found Trade J.*, 1951, **91,** Nov. 22, 585–593). Practical details are given of the methods used at the foundry of Parsons and Co., Ltd., for moulding, drying, placing of chills, and dust suppression. In the discussion the author deals with sand loss and the effects of mechanization of founding.—E. T. L.

Builders' and Engineers' Castings. (*Foundry Trade J.*, 1951, **91,** Oct. 4, 391–394). This is a description of the range of work, and the layout and equipment at the Watford Foundry Company's works.—E. T. L.

Osborn's Steelfoundry Extension. J. Preston. (*Found. Trade J.*, 1951, **91,** July 12, 41–45). *See* " Steel Foundry Progress : Reorganization by Osborn Foundry," *J. Iron Steel Inst.*, 1952, **170,** Jan., 69.

Foundries in the French Ardennes. A. R. Parkes. (Inst. Brit. Foundrymen : *Foundry Trade J.*, 1951, **91,** Nov. 8, 525–529 ; Nov. 15, 565–573). Six foundries were visited by a party from the Inst. Brit. Foundrymen, and this is a report of notable points. At the Faure et Cie works there is a novel suspended-roundabout system of materials flow. As well as giving details about the foundry techniques and output at each works, the author mentions the Ardennes communal testing laboratories.—E. T. L.

Mechanized Small Foundry. (*Canad. Metals*, 1951, **14,** Aug., 13–14, 16). A brief account is given of the layout and materials handling system at the small new foundry of Crouse-Hinds Co., Toronto. High output is achieved by fullest utilization of mechanical handling.—E. C.

Draft Specification for Classification of Casting Defects. A. Plešinger. (*Hutnické Listy*, 1951, **6,** 6, 262–270). [In Czech]. A specification for classifying casting defects is proposed.

Defects in Castings. I—Causes of Defective Shapes. J. Drachmann. (*Gjuteriet*, 1951, **41,** Nov., 172–174). [In Swedish]. This is the second list of castings defects classified by the Swedish Standards Committee.—B. S. E.

Defects in Castings and Their Causes. II—Non-Destructive Testing Methods for Castings Control. L. Barrling. (*Gjuteriet*, 1951, **41,** Nov., 161–171). [In Swedish]. The author discusses the principles of the more important non-destructive testing methods, including magnetic crack testing and the use of X-rays and gamma rays.—B. S. E.

Contraction and Blowholes. J. Leonard. (Assoc. Techn. Fonderie : *Foundry Trade J.*, 1952, **92,** Jan. 24, 95–98). The author proposes standard terms for the results of contraction in casting. The four main causes of blowholes are listed, and the various types of hole are described and related to gas porosity and remedies.—E. T. L.

System of Studying Casting Defects. G. W. Nicholls and D. T. Kershaw. (*Inst. Brit. Found.*, 1951, June 12–15, Preprint No. 1003 : *Found. Trade J.*, 1951, **91,** Oct. 4, 383–390 ; Oct. 11, 423–430). The authors attack the idea that defective castings are to be expected. They outline the value of record cards, staff training, and the importance of camber. The second part deals with gating, pouring, drying, melting, and ladles.—E. T. L.

Repair of Castings with Synthetic Resins. K. Holeš. (*Hutnické Listy*, 1951, **6,** 5, 229–31). [In Czech]. Tests lasting six months showed that only certain bakelite resins are suitable for rendering porous castings serviceable. The resin is introduced into the castings either by a vacuum or by compressed air. Both methods are described.—E. G.

" Spec " Sheets and Their Various Uses. J. Taylor. (*Trans. Amer. Found. Soc.*, 1951, **59,** 372–375). One particular type of foundry record card is described, and the advantages of keeping a full set of records are discussed.—P. C. P.

Metal Penetration. M. E. Nixon. (*Canad. Metals*, 1951, **14,** Aug., 42–47). Basic causes of metal penetration into moulding sands are described. Liquid metal penetration is regarded as more troublesome than oxide penetration, the significance of the latter still being in doubt. Measures to prevent penetration are discussed.—E. C.

Compressed Air Installations in the Foundry. K. Stockkamp. (*Giesserei*, 1951, **38,** Dec. 13, 637–646). Types of compressor most suitable for foundries are described, and data are given of power and cooling-water consumptions of compressors. Formulæ, tables, and graphs are provided for the selection of sizes of compressors and pumps.—J. G. W.

Dust Control at Ontario Malleable. H. N. Acker. (*Canad. Metals*, 1951, **14,** Aug., 22–24, 28). Complete elimination of dust nuisance has been achieved in one foundry with a ' Dustube ' collecting system installed by American Wheelabrator and Equipment Co. The collector comprises a system of cloth tubes to strain the air. Foundry operations kept free from dust include sand ramming, tumbling, grinding, and sand reconditioning.—E. C.

Dust in Steel Foundries. (Factory Dept. Ministry of Labour and National Service, 1951, H.M. Stationery Office). This is the second report of a committee appointed by the Factory Department of the Ministry of Labour and National Service to consider methods of preventing the production or inhalation of dust, and the possibility of reducing the use of materials containing free silica in steel foundries.—T. E. D.

Observation and Control of Dust in Foundry Dressing Operations. Part I—Control of Dust. R. F. Ottignon. (*Inst. Brit. Found.*, 1951, June 12–15, Preprint No. 1008 : *Found. Trade J.*, 1951, **91,** July 26, 99–104). *See J. Iron Steel Inst.*, 1952, 170, Jan., 69.

Observation and Control of Dust in Foundry Dressing Operations. Part II—Observation of Dust. W. B. Lawrie. (*Inst. Brit. Found.*, 1951, June 12–15, Preprint No. 1008 : *Found. Trade J.*, 1951, **91,** Aug. 2, 129–137 ; Aug. 16, 181–185). Details are given of the photographic arrangements used in obtaining the illustrations of the flow and amount of

dust from a pneumatic chisel, an abrasive wheel, a fettling bench, and two grinders. The technique is suitable for works use, and the results help to improve dust control.—E. T. L.

Safety Precautions for Special Work. H. Allen. (*Foundry Trade J.*, 1952, **92,** Jan. 24, 93–94). The author deals with preventing accidents connected with the employees of outside contractors in a foundry. Topics touched on include liability, equipment, and supervision.—E. T. L.

British Foundry Training Facilities. V. C. Faulkner. (*Foundry Trade J.*, 1951, **91,** Aug. 16, 177–179). The author describes the scope of the City and Guilds examinations, the British Foundry School at Wolverhampton, the National Foundry Craft Training Centre at West Bromwich, and the foundry schools of Newton Chambers Ltd., and the Meehanite Metal Corp.—E. T. L.

HEAT-TREATMENT AND HEAT-TREATMENT FURNACES

Heat-Treatment of Grey Cast Iron. Sub-Committee T.S.31. (*Inst. Brit. Found.*, 1951, June 12–15, Preprint No. 1012: *Found. Trade J.*, 1951, **91,** Aug. 2, 117–124). This report deals with annealing for improved machinability, and for the removal of chill, with heat-treatment to improve hardness and strength, with stress-relief, pre-enamelling treatment, and miscellaneous treatments. The committee makes recommendations on desirable methods of giving these heat-treatments to grey cast iron.—E. T. L.

Investigations into Annealing from the Temperature of Hot Working with Isothermal Transformation. E. Theis. (*Stahl u. Eisen*, 1951, **71,** Dec. 20, 1433–1438). Using bearing steel and high-carbon structural steels, tests have been carried out into annealing from the temperature of hot working with isothermal transformation in the Ar_1 region. The transformation behaviour with different hot-rolling temperatures (750, 850, and 950° C.) and holding temperatures and times in the furnace have been followed by hardness measurements and structural examination. For nickel-free steels, the most suitable holding temperature is 700° C.; for high-nickel steels it is 630–650° C. Although transformation is not complete even after 18 hr. in the furnaces, tensile strengths after 1–3 hr. allow satisfactory machining, provided that the requirements for machinability and cold workability are not too severe. Tensile strengths under 70 kg./sq. mm. can be obtained. Annealing from the finishing temperature can be employed with advantage with nickel-rich steels.—J. P.

Soft Annealing of High-Carbon Steels with Isothermal Transformation. W. Hülsbruch and E. Theis. (*Stahl u. Eisen*, 1952, **72,** Jan. 31, 123–133). Annealing methods for obtaining a uniform structure with spheroidal cementite in bearing steels are quoted. The most convenient annealing procedure using different temperatures, times, and cooling rates on steels with 1·0% C and 1·0% Cr was studied, and the special dilatometric method for determining transformation points is described. These tests clarified the course of transformation and indicated the possibility of destroying grain-boundary cementite and of ensuring routine production of the desired microstructure with spheroidal cementite. These facts have enabled a new type of annealing to be introduced for which the name 'annealing with isothermal transformation' (Glühung mit isothermische Rückumwandlung) is proposed. The process consists in holding briefly at temperatures above the Ac_1 point up to 60° C. above Ac_3, cooling rapidly to between Ar_3 and Ar_1, isothermal treatment at a favourable temperature until transformation is complete, and finally cooling at any desired rate. The method has qualitative and economic advantages. Its applicability to alloyed and unalloyed steels has been investigated. The method has been found very suitable for alloy steels with above 0·5% C and for hypereutectoid unalloyed steels. In order to reap full advantage from the method, special furnaces are necessary; long continuous furnaces with annealing, cooling, and isothermal holding zones appear to be suitable.—J. P.

FORGING, STAMPING, DRAWING, AND PRESSING

Cold Forming Steel Sections. R. Saxton. (*Metallurgia*, 1951, **44,** Dec., 285–286). Factors influencing the efficient reduction of steels in cylindrical form to various shapes and segments of small cross-sectional area by cold processing are discussed. Reference is made to hot drawing, which gives a higher output with decreased production costs.—B. G. B.

Deep Drawing with 'Rubber Dies.' F. Young. (*Modern Metals*, 1951, **7,** May, 28–30). A process developed by Glenn L. Martin and Hydropress allows more complex deep drawing by utilizing a thick rubber pad in lieu of the steel female die. T. E. D.

Contribution to the Problem of the Mechanical Ageing of Hard-Drawn Patented Steel Wires. F. Schwier. (*Stahl u. Eisen*, 1952, **72,** Jan. 17, 58–66). The influence of time and temperature on the strain-ageing of patented and drawn steel wires has been investigated. Tests were also carried out to determine whether the temperatures produced during drawing were such as to accelerate ageing. Previous investigations are reviewed and the importance of the stress/strain diagram for various types of steel and its dependence on ageing processes are discussed. In wire-drawing, particularly on multiple-draw machines, adequate cooling is of great importance, if ageing is to be avoided.—J. P.

Measuring and Manufacturing Methods for Drawing Dies with Pre-Determined Rounding-Off Radii and Bearing Length. S. Werth. (*Stahl u. Eisen*, 1952, **72,** Jan. 17, 66–69). Differences in bearing length, determined with the two-needle Zetmeter apparatus of Lueg, of a die with sharp-edged profile and with the edges rounded off, can be used to calculate the rounding-off radii and the true bearing length. It is possible to test and to conform to predetermined dimensions without appreciable expense by intermediary measurements during manufacture. Determination of rounding-off radii on the finished die is not possible without these previous measurements.—J. P.

ROLLING-MILL PRACTICE

Output and Efficiency of Cold Rolling Mills by a Graphical Method of General Validity. W. Lueg. (*Stahl u. Eisen*, 1952, **72,** Jan. 17, 75–79). The rolling-time formula derived by Pomp is presented in a nomographic form of general validity, and the use of the nomograms is illustrated by several examples. The effect of mill efficiency on the economics of rolling is discussed and the corrections for applying the nomograms to the rolling of all metals are tabulated.—J. P.

Effect of Coil Weight and Rolling Speed on the Hourly Output of Cold Rolling Mills. H. Panneck. (*Stahl u. Eisen*, 1952, **72,** Jan. 17, 70–75). Output diagrams can be drawn up in a simple way for all cold-rolling mills and rolling methods. These diagrams indicate the effect of coil weight and rolling speed on the output. With these the operative can determine the correct procedure for improving the output of a mill. The optimum coil weight and rolling speed can also be predetermined for new mills. According to waste diagrams, coil weights for rolling thicker sections should be at least 3–4 kg./mm. of strip width. The rolling speed should not be too high, since otherwise the mill will not be utilized to its maximum. With thinner sections, end-losses are tolerable even with coil weights of 2–3 kg./mm. strip width. The rolling speed in this case can be as high as possible so as to obtain a good hourly output. Similarly, with multi-stand tandem mills, it is better to increase the rolling speed than the coil weight.—J. P.

A New Method of Making High-Pressure Drums. J. Nesvadba. (*Hutnik*, (Prague), 1951, **1,** 12, 270–271). The Röckner method of hot-rolling high-pressure tubes from hollow-forged billets is described. The billet is slid on to the mandrel, which can rotate and is parallel to and co-planar with the axes of two rolls, one above and the other below the billet. In the rolling process the billet elongates and its wall thickness decreases simultaneously. At a certain reduction in thickness the billet travels along the spindle, which is common to a series of pairs of rollers, to the next pair, which reduces it further. The flow, unlike that in forging, takes place in the direction of the neutral fibre, and is therefore uniform. Other methods based on the same principle are described.—P. F.

Modern Electric Control Apparatus and Drives for Rolling-Mill Trains. H. Opitz. (*Stahl u. Eisen*, 1952, **72,** Jan. 3, 12–19). The types of control equipment now available for mill trains and for new and reconstructed rolling mills are discussed. Units for use in transmitting signals to the control apparatus include the following types of amplifier: machine (Amplidyne and Rototrol); electronic (Thyratron, Ignitron, and grid-controlled rectifiers); magnetic; and electrohydraulic. The characteristics of these amplifiers and the ways in which they may be employed are dealt with.—J. P.

MACHINERY FOR IRON AND STEEL PLANT

Power Station at a Large Steelworks. (*Elect. Rev.*, 1951, **149,** Aug. 10, 263–269). The new power station erected at the steelworks of the Consett Iron Co., Ltd., is described. It provides not only electricity but also cold air under pressure, and process steam. The design allows the use of three fuels, blast-furnace gas, coke-oven gas, and coal, singly or in any combination, and either pulverized fuel firing or stoker firing can be used for the solid fuel. Two 15,000-kW. Parsons turbo-alternators have been installed, and a third set will be installed later.—T. E. D.

Influence of Bearing Design on Load Carrying Capacity and Safety of Operation of Bearings. A. Buske. (*Stahl u. Eisen*, 1951, **71,** Dec. 20, 1420–1433). As a result of practical tests and theoretical considerations, rules for the design of safe bearings have been formulated. These are presented and discussed.—J. P.

WELDING AND FLAME-CUTTING

The Butt Welding of Rail Joints. E. Henrion. (*Rev. Soudure*, 1951, **7,** 4, 195–204). The advantages of welding rail joints are discussed. A method of oxy-acetylene welding by two welders, one on each side of the rail, is described. This method gives excellent results, prevents distortion, and speeds up the process.—M. D. J. B.

Suitability of Steels for Flash Butt Welding. E. Hörmann. (*Stahl u. Eisen*, 1952, **72,** Jan. 3, 19–24). Results of tests on flash butt welds on alloyed and unalloyed steels are reported. These show that, if certain precautions are observed during welding and subsequent heat-treatment, high-grade welds can be made by this process with different types of steel. Only steels with high contents of silicon or aluminium are unsuitable. Working temperatures must not be too high if cracking near the weld is to be avoided. Internal microruptures in the basis metal may occur if the pressures are too low and the welding time is too long. For jobs with heavy sections and wall thicknesses, preheating should be employed wherever possible. Pressures of 2–4 kg./sq. mm. are satisfactory for unalloyed steels; for alloyed materials 6 kg./sq. mm. is recommended.—J. P.

Electric Furnace Brazing Provides High Production Rate at Low Cost for Superweld Corp. (*Indust. Heating*, 1951, **18,** Aug., 1356–1368, 1506–1510). In this well-illustrated article a furnace installation at the Superweld Corporation, California, is described, which is used for joining steel stampings and many other component parts. The installation consists of two furnaces rated at 320 and 88 kW., respectively.—J. A. L.

MACHINING AND MACHINABILITY

Calculation of Optimum Radius of Curvature of the Feeler Tip in the Measurement of Surface Waviness. T. S. Lopokov. (*Stanki i Instrument*, 1950, No. 4, 24–25). [In Russian].

Influence of Tool Wear on the Microgeometry of the Surface. P. P. Grudov and Kh. V. Levant. (*Stanki i Instrument*, 1950, No. 4, 17–18). [In Russian]. In the investigation described, surfaces of grey cast iron and steel were machined at various speeds but under otherwise constant conditions until complete failure of the cutting tool occurred, the quality of the surface being determined at various stages of machining. For the cast iron, surface quality deteriorated continuously with increasing tool wear and with increasing speed of cutting at a given stage of tool usage. For the steel, surface quality at first improved with tool wear, then deteriorated, and finally improved again.—S. K.

Visual and Optical Evaluation of Metal Surfaces. H. Thielsch. (*Metal Finishing*, 1951, **49,** May, 54–61). Assessment of roughness of metal surface by sight, microscopic inspection, replica techniques, electron microscopy, sectioning, and interferometry are discussed.—J. P.

Dependence of the Quality of a Ground Surface on the Speed of the Grinding Wheel. D. M. Tarasenko. (*Stanki i Instrument*, 1950, No. 4, 19). [In Russian]. In the investigation described, steel specimens, preliminarily ground under standard conditions, were ground with peripheral wheel velocities of 11 to 50 m./sec. The profilograms show that as the wheel speed gradually increases, the surface quality in both directions continuously improves.—S. K.

Microgeometry of a Surface during the Internal Grinding of Tempered Steel. A. B. Kondrat'ev. (*Stanki i Instrument*, 1950, No. 4, 20). [In Russian]. Steel rings with internal diameters of 110 mm. were internally ground with a frequently dressed electro-corundum wheel under various conditions, the corresponding surface qualities (as indicated by the roughness perpendicular to the direction of grinding) being determined.—S.K.

Russian Work on Surface Quality. P. E. D'yachenko (*Stanki i Instrument*, 1950, No. 4, 4–9). [In Russian]. This is a review of work carried out in the U.S.S.R. on the standardization of measures of surface quality and the methods of its determination.—S. K.

Surface Finish. R. E. Reason. (Inst. Engineers, Australia: *Australasian Eng.*, 1951, Oct. 8, 48–59). The author discusses the nature and types of surface, and various methods of measuring surface finish are reviewed, among them the method of taper sectioning, the carrier modulating and generating types of stylus instrument, and optical interference methods. Numerical assessment of surfaces is discussed, particularly the Swedish and German peak-to-valley measures, the British centre-line-average, the American root-mean-square, and crest-line and root-line measures. Methods of calibrating surface-finish measuring instruments are described.—P. M. C.

Thread Cutting on Austenitic Steel Parts. N. N. Zorev. (*Stanki i Instrument*, 1950, No. 4, 15–17). [In Russian]. The special measures to control cutting conditions during thread cutting, made necessary by the poor machinability of austenitic steel, are outlined. An optimum cutting speed of 1–2 m./min. was established.—S. K.

The Machinability of Alloy Steels in Fine-Finish Turning. G. Wagner and P. Wiest. (*Stahl u. Eisen*, 1951, **71,** Nov. 22, 1317–1323). In order to assess the value of machinability tests, 23 alloy steels were investigated by three methods: (1) Measurement of the cutting speed, under standardized conditions, at which the tool gave a cut of 100 m. length before failure or at which the tool had a life of 1 min. (2) The cutting speed increment method, in which the speed was increased in uniform steps; the speed at which the tool fails is a measure of the machinability. (3) Measuring the cutting temperature at a speed of 15 m./min. Only the second version of the first test and the speed-increment method were of value as rapid procedures. Both were simple to carry out. An alloy steel has optimum machinability when the carbides are fine, spherical, and uniformly distributed in a ferritic matrix.—J. P.

Cratering on Carbide Tools. E. M. Trent. (Inst. Mech. Eng.: *Mech. World*, 1951, **130,** Nov. 30, 502–504). A new theory based on observation of conditions at the tool tip is put forward to account for cratering on carbide tools. Under the heat of friction, an alloy is formed between the steel and tungsten carbide with a melting point lower than that of either.—D. H.

Tool Wear Results from Several Causes. M. C. Shaw and P. A. Smith. (*Machinist*, 1951, **95,** Dec. 8, 1868–1871). Wear on the clearance face is the combined effect of pressure welds, temperature welds, and the lapping action of hard particles in the work material. The degree of wear from the first two causes is a function of cutting speed. At some speeds wear is accelerated as the tool matrix loses hardness relative to the workpiece matrix.—E. C. S.

Microstructure and Machinability. G. Weyer. (*Z.V.d.I.*, 1951, **93,** Dec. 1, 1076–1077). Collating the results in several papers, the author points out that machinability of cast irons correlates inversely with Brinell hardness and improves with the amount of ferrite present. The machinability index is not, however, an absolute quantity; it depends also on the tool material, and results quoted for three grades of carbide tool showed an unexpected optimum machinability for a Widmanstätten structure. Nodular cast iron has superior machinability.—J. G. W.

CLEANING AND PICKLING

Cleaning of Steel Test Panels for Paint. T. Rice. (*A.S.T.M. Bull.*, 1951, Dec., 50–58). The basic cleaning methods adopted were solvent spray cleaning, trichlorethylene vapour degreasing, and modifications of these using a phosphoric acid dip. Solvent wipe procedures were found unreliable. Photographs show comparison of panels cleaned by solvent wipe and trichlorethylene degreasing when subjected to distilled water and 20% salt solution immersion.
B. G. B.

Fitting Vapour Degreasers to the Job. G. C. Close. (*Products Finishing*, 1952, **16**, Jan., 32–38). Some advice is given on the use of solvent degreasers and the types of equipment for various applications.—J. P.

Cyanides and The Waste-Disposal Problem. G. T. Long. (*Indust. Heating*, 1951, **18**, Oct., 1744–1748, 1922; Nov., 1994–1998). After pointing out the harmful effects of waste discharge into rivers and the atmosphere, the author lists some of the more common waste products and goes on to deal with cyanide salt wastes and methods of testing in order to control alkalinity.—J. A. L.

PROTECTIVE COATINGS

Inspection of Electroplated Aircraft Parts. P. Skeggs. (*J. Electrodepositors' Tech. Soc.*, 1952, **28**, 15–26). The general inspection requirements of D.T.D. specifications covering plating of aircraft parts are outlined. Sampling and methods of testing are dealt with generally; the particular requirements of specifications for chromium, nickel, silver, and rhodium plating and surface treatments of zinc and cadmium are dealt with in more detail.—J. P.

Problems of Plating Powder Metal Parts. J. D. Shaw, W. V. Knopp, and C. L. Clark. (*Metal Finishing*, 1951, **49**, Nov., 56–58). Some of the difficulties in plating sintered metal powder components and the methods adopted to overcome them are described.—J. P.

Dragout Control. J. B. Kushner. (*Metal Finishing*, 1951, **49**, Nov., 59–61, 64). The factors responsible for dragout are discussed mathematically and an equation is derived relating the amount of dragout to withdrawal velocity and kinematic viscosity of solutions.—J. P.

Metal Finishing Developments in 1951. W. A. Raymond. (*Metal Finishing*, 1952, **50**, Jan., 50–56). Research and development work carried out during the past year is reviewed. The topics discussed include: Porosity, stress, hardness, orientation, and brightness of electrodeposits; electrolytic and chemical polishing; scale removal and acid dipping; hydrogen diffusion; copper, nickel, chromium, zinc, tin, silver, and alloy plating; anodized and conversion coatings; chromizing; testing and analysis; equipment; and cleaning and degreasing.—J. P.

The Control of Bright Zinc Plating. F. J. Kolar, jun. (*Metal Finishing*, 1951, **49**, Nov., 52–55). It is recommended that the practice of controlling the cyanide/zinc ratio should be abandoned and analysis conducted for total caustic, total cyanide, and total zinc contents. Brighteners should not be added to zinc baths but reliance placed on subsequent bright dips. A method for determining the sulphide content of zinc plating baths and a quality control procedure are described.—J. P.

Finishing Precision Aircraft Accessories. G. C. Close. (*Products Finishing*, 1951, **16**, Dec., 14–20). The methods employed by Air Research Manufacturing Co., Los Angeles, are exemplified by a description of the surface preparation, anodizing, cadmium plating, and painting of the components of a small air expansion turbine.—J. P.

Protective Coatings Used on Gas Pipe. R. T. Richards and N. K. Senatoroff. (*J. Amer. Water Works Assoc.*, 1951, **43**, Dec., 1015–1020). Experiences of the Central Arizona Light and Power Co. and the Southern Counties Gas Co. of California are outlined. The most satisfactory methods of applying coal-tar enamel coatings for various soil conditions are described.—T. E. D.

Flame-Sprayed Plastic Coatings. B. Goldberg. (*Corrosion*, 1951, **7**, Feb., 47–50). The development of flame-spraying is outlined, and equipment, techniques, and materials are discussed. Problems in producing suitable powdered plastics are reviewed and developments in uses of polythene compounds, fluorinated hydrocarbons, and 'hot melt' compositions for non-porous coatings, are described.—E. C.

Hardness of Sprayed-Metal Coated Surfaces and Effect of Hardness on Wear Resistance. V. A. Shadrichev. (*Vestnik Mashinostroeniya*, 1948, **28**, 11, 21–23). Investigations of the influence of metal-spraying practice on the hardness and wear-resistance of coatings are described.—V. G.

Vacuum Metallising. P. Rosenblatt. (*Machine Design*, 1951, **23**, Oct., 141–144, 180–181). Vacuum coating is most useful in the application of metallic surfaces to materials which are non-conductors of electricity. The materials which have been successively metallized include glass, metal, paper, plastics, cloth, wax, inorganic crystals, and most lacquered surfaces. A variety of films is possible, and the process often produces a superior product at lower cost than other metallizing methods.—E. C. S.

New Methods of Metal-Spraying. H. Reininger. (*Metalloberfläche*, 1950, **4**, July, A105–A107). Instead of the metal-base/sprayed-metal system, an intermediate layer of nickel can be sandwiched between the steel base and the sprayed metal. Much greater adhesion is attained. An improvement developed by J. Frank of the Metallizing Engineering Co., New York, is described. A rough deposit of another metal on a steel surface is obtained by pressing an electrode of that metal against the steel surface and passing a current from electrode to steel so that the electrode melts at hot spots in the contact interface, thus depositing a rough layer on to which the final surface is sprayed. In the Colmonoy method a metal powder, melted in its passage through an oxy-acetylene flame, on leaving the spray gun, is deposited on a sand-blasted surface, and great adhesion is attained by allowing the deposit to melt and diffuse partially into the metal base by heating at 1000° C. A very hard alloy steel surface can then be deposited on this surface.

On the Metallurgy of Metal Spraying. K. Krekeler. (*Metalloberfläche*, 1950, **4**, Oct., A151–A153). Metallurgical features involved in metal spraying are discussed. Adhesion and bending strengths of 0·04-in. zinc layers were best if the steel surfaces were roughened by sand-blasting with 0·4–0·8-in. grains. Coarser sand or steel pellets were inferior. Relations between layer thickness and bending strength and adhesion respectively are plotted, spraying conditions being specified. Micrographs showing spraying defects due to oxygen inclusion, too high a wire velocity in the spray gun, and excess acetylene, are shown.—P. F.

Metal-Spraying and Its Applications In Mining. P. Chlebus. (*Glückauf*, 1951, **87**, Sept., 875–882). The history of metal-spraying is sketched. Available German types of spray gun and their performances are described, and the physical and chemical processes involved in metal spraying are discussed. Examples of the economies attainable by metallizing mining gear and transport, particularly for corrosion protection, are presented.—P. F.

Phosphate Coatings in Defence Production. A. Douty. (*Metal Finishing*, 1951, **49**, July, 105–108, 120). The use of phosphate conversion coatings for bonding paint to iron, zinc, cadmium, aluminium, and their alloys, for rustproofing iron and steel with or without the aid of corrosion-preventive oils, for protecting friction surfaces of ferrous metals, and for improving cold drawing, extrusion, and forming of steel, is discussed.—J. P.

Vitreous Enamelling Cast Iron and Steel. J. W. G. Pedder. (*Times Rev. Ind.*, 1952, **6**, Feb., 22–24). The development of cleaning, including 'airless' shot blasting, is reviewed. The advent of wet process enamels widened the field of vitreous enamelling. Typical formulæ for frits for the wet and dry processes are given.—T. E. D.

Investigations of the Porosity of Acid-Resisting Enamel Coatings. K. Frick. (*Metalloberfläche*, 1950, **4**, July, A97–A101). Experiments on enamelled goods subject to a fluid pressure of 13 atm. showed that gases and liquids can travel within an enamel layer parallel to the surface. This occurs only if an undercoating of sintered enamel is used, such as is customary with cast-iron objects. If the enamel is applied in the liquid state, as is the case in coating steel, it is liquid and gas tight.—P. F.

Recent Developments in Ceramic Coatings for Steel. A. G. Gray. (*Products Finishing*, 1951, **16**, Dec., 44–74). Recent work in America on the adherence and resistance to weathering and abrasion of porcelain and other ceramic coatings on steel is reviewed.—J. P.

Application of Dilatometric Analysis to the Problem of Enamelling Cast Iron. A. Le Thomas and P. Tyvaert. (Assoc. Techn. de Fonderie: *Foundry Trade J.*, 1952, **92**, Feb. 7, 151–155). The authors emphasize that some agreement between the expansion coefficients of cast iron and its enamel coating is necessary for adhesion. A technique is described for measuring the coefficients, using a Chevenard differential dilatometer.—E. T. L.

The Protection of Iron by Painting. M. Ragg. (*Werkstoffe u. Korrosion*, 1952, **3**, Jan., 11–17). The author reviews the theory and practice of the protection of structural steelwork

by painting. The formulation of paints, their physical properties, and the effects of surface preparation for painting are considered. Soap formation is an important factor in determining inhibition by priming paints, and the excellent protective properties of red lead paints are largely due to the improved weather-resistance of the paint film resulting from the gradual formation of lead soaps within it.—J. C. H.

The Problem of Painting Bright Chrome Plate. W. D. McMaster. (*Plating*, 1951, **38**, July, 696–698, 703). The conditions conducive to satisfactory adhesion of paint, lacquer, and enamels to bright chromium plating have been determined by experiment. They include careful control of the plating bath, adequate cleaning if the parts have been buffed, and a hot chromic acid dip.—J. P.

PROPERTIES AND TESTS

Apparatus for Low Temperature Tension Tests of Metals. R. J. Mosborg. (*A.S.T.M. Bull.*, 1951, Oct., 41–44). The tests were conducted in a 120,000-lb. hydraulic testing machine. Liquid nitrogen was used for tests at − 312° F. and Freon 12 cooled with liquid nitrogen for tests between − 90° and − 230° F. Liquid nitrogen was stored in Dewar flasks between tests. To record the applied load an extensometer with two dials gave an average value of the existing elongation. The temperature of the specimen was measured and recorded continuously by a self-balancing potentiometer.—B. G. B.

Influence of Temperature on the Elastic Constants of Metals and Alloys. G. Vidal, P. Lescop, and L. Raymondin. (*Rev. Mét.*, 1951, **48**, Nov., 864–874). Since the fundamental elastic constants are related by the equations $1 + \sigma = E/2G$ and $E = 3K(1 - 2\sigma)$, it is only necessary to determine two of the constants. Young's modulus E is measured by Florisson's vibration method, and σ is obtained indirectly by Kirchoff's method. The effect of temperature on E, for pure metals, ferritic steels and austenitic steels, and on σ (Poisson's coefficient) for ferritic and austenitic steels has been studied.—A. G.

Flow and Relaxation of Drawn Wires. R. de Strycker. (*Rev. Mét.*, 1951, **48**, Nov., 888–893). Relaxation is measured by rapidly bringing tension up to its initial value, maintaining it for 2 min., and then varying it to keep the specimen length constant. The optimum specimen length, scatter of results, and the effect of natural and artificial ageing on relaxation are considered.—A. G.

Reproducibility of Bend Test for High Hardness Steels. L. D. Jaffe and D. C. Buffum. (*A.S.T.M. Bull.*, 1951, Oct., 36–37). High-carbon alloy steel specimens were given a single heat-treatment that produced a Rockwell hardness of C52½. The strength in bending was determined by breaking under two-point loading. Statistical methods were used to determine the number of tests required to show which of two specimens was the stronger ; six tests are sufficient for material differing in bend strength by 5% or more, and two or three tests when differences of 10% or less are not of interest.

B. G. B.

A New Method for the Micromechanical Testing of Metals. N. Mironoff. (*Rev. Soudure*, 1951, **7**, 4, 214–232). The method described consists of a modified and improved bend test in which the test piece is submitted to two opposed couples. A study is made of the geometric deformations of test pieces ; it is shown that the neutral fibre retains its original length for all angles of bend. The accuracy of the test is discussed. The effects of heat-treatment and plastic behaviour of steels and the effects of welding on parent metal can be studied with this test.—M. D. J. B.

The Influence of the Surrounding Medium on Plastic Deformation of Metals. G. Masing. (*Met. Ital.*, 1951, **43**, Nov., 467–470). [In French]. The author confirms the results obtained by workers of the P. Rehbinder school of thought on the influence of the surrounding medium on the deformation of metals. There is no clear evidence of the influence of the medium on electrical resistance. The paper accepts the fundamental theory of Rehbinder but not his somewhat revolutionary results.—M. D. J. B.

Results of Fatigue Tests under Progressive Loading. M. Prot. (*Rev. Mét.*, 1951, **48**, Nov., 822–824). When several specimens of the same metal are tested at different values of α (rate of increase of load with time) and $\sqrt{\alpha}$ is plotted against the rupture stress, a straight-line relationship is obtained, the point of intersection with the ordinate defining the limit of endurance. The method gives a gain in time of 90% over ordinary tests, and, with certain exceptions, is in excellent agreement with them.—A. G.

The Fatigue of Metals. M. Roš. (*Met. Ital.*, 1951, **43**, Dec., 512–520). The author examines the fatigue limit for different monoaxial stresses in relation to the notch coefficient

$$\alpha_{max} = \frac{\text{max. stress in notch, } \sigma_{max}}{\text{mean stress in section, } \sigma_m}$$

The influence of the stress gradient, notch size, and state of internal tension is examined. The results of tests on materials free from defects, almost homogeneous, and almost isotropic, are given.—M. D. J. B.

Testing the Hardenability of Constructional Alloy Steels. M. Kroneis and H. Krainer. (*Stahl u. Eisen*, 1951, **71**, Dec. 6, 1365–1375). Investigations have been carried out on chromium–molybdenum and chromium–vanadium steels to explain the scatter of test results in the end-quench test. Frequency curves show that the test, on one material and in one laboratory, gives values with excellent reproducibility and from this point of view is to be regarded as the most useful method for characterizing the hardenability of medium alloy structural steels. End-quench tests and isothermal 'disc' tests have been performed on five alloy steels (0·25–0·4% C ; 0·3–1·25% Si ; 0·6–1·8% Mn ; 0 or 0·8% Al ; 0–2·4% Cr or 0·2% Mo, and 0–0·2% V) whose isothermal transformation diagrams had been evaluated. In some cases, the ideal critical diameter had been calculated from the composition by Grossmann's method. The disc method gives satisfactory agreement with the end-quench results, and allows the change of hardenability over the cross-section to be followed in a very simple manner. It is also suitable for detecting segregation. There is less satisfactory agreement with the calculated ideal critical diameter, but this does not agree even with the end-quench results. Both tests are suitable for assessing the influence of hardening temperature and holding time. The disc test consumes less material and costs less than the end-quench test.—J. P.

Application of Meyer Microsclerometric Analysis to Temper Brittleness. H. Bückle. (*Rev. Mét.*, 1951, **48**, Nov., 858–863). The factors associated with temper brittleness are : (*a*) Presence of internal stress ; (*b*) reversibility ; (*c*) instability of reversibility at certain temperatures ; (*d*) retarding influence of certain elements ; and (*e*) small difference between microscopical appearances and the value of 'n' in Meyer's Law $P = cd^n$ for the strong and brittle states. These are explicable by a reversible reaction between the ferrite matrix and various carbides whose determining mechanism would be the diffusion of carbon.—A. G.

Micrographic Study of Temper Brittleness in Low Alloy Carbon Steels. P.-A. Jacquet. (*Rev. Mét.*, 1951, **48**, Nov., 825–852). The fragility appearing at about 500° C. in Ni–Cr or Cr–P steels is associated with a continuous network of primary austenite grain boundaries. The structural evolution in Ni–Cr and Ni–Cr–Mo steels on quenching and annealing at 500° and 620° C. are studied microscopically and the fractures of impact specimens of these steels compared.—A. G.

Study of Temper Brittleness in Certain Steels by X-Ray Diffraction. Adrienne R. Weill. (*Rev. Mét.*, 1951, **48**, Nov., 853–857). Such brittleness depends at least in part on the state of crystallization of the lattice. Three steels were studied with the following results : (*a*) The variations in brittleness of Ni–Cr steels affected the reflection diagrams appreciably ; (*b*) the smaller variations in brittleness of Ni–Cr–Mo steels corresponded to very different effects in these diagrams ; and (*c*) for chromium steels there was little difference in diagrams of the strong and brittle states.—A. G.

Friction and Wear with Reference to the Physics of Surfaces. A. Marcelin. (*J. Phys. Radium*, 1951, **12**, Oct., 1A–16A). The author points out that friction depends on surface roughness, (the latter decreasing with wear), and then describes experiments where both of these were measured. Wear only occurs with metal surfaces if they are separated by a 'stratofilm' of two layers of lubricant a few molecules thick, firmly attached to the respective surfaces. The apparatus used in this study consisted of a sphere rubbing along a cylinder under various loads, and making several cycles per second. The variables studied were the lubricant, the state of the surfaces, and the choice of metals. The results showed that, whereas dry friction was usually accompanied by a transfer of metal from one surface to the other, this never occurred when the rubbing took place in an oil-bath.

Periodic Potential in Metals. S. Chiba and Y. Shiota. (*Sci. Rep. Tôhoku Univ.*, 1949, **33,** Apr., 64–69). [In English]. Fourier coefficients of periodic potential in metallic crystals of lithium, sodium, iron, and copper are calculated by Bethe's method. Details are given for the case of metallic iron as an example of the calculation.—R. A. R.

Magnetostriction in Weak Magnetic Field. S. Matsumae. (*Sci. Rep. Tôhoku Univ.*, 1950, **34,** Nov., 129–139). [In English]. The longitudinal magnetostriction in the initial permeability range has been studied by capacity bridge and mutual dynamic impedance methods using specimens of electrolytic iron and nickel. The apparatus is described. Results by the former method indicate that longitudinal magnetostriction exists in nickel but not in iron.—R. A. R.

Development of Methods for Testing Ferromagnetic Materials. W. Jellinghaus. (*Arch. Eisenhüttenwesen*, 1951, **22,** Nov.–Dec., 401–409). Developments from 1939 to 1951 in ferromagnetic testing are reviewed. Induction and permeability measurements on magnetically soft materials have been increasingly carried out in alternating fields, using phase-sensitive rectifiers and D.C. voltmeters. In the measurement of watt loss, the tendency has been to use smaller samples. Where the voltages are too small, because of the small size of the specimens, valve amplifiers have been inserted between the secondary winding and the volt- or watt-meter. The development of materials of high permeability for transformers has led to the construction of testing equipment for complete cores. There has been a marked improvement in quality of the Fe–Ni–Al alloys for magnets, and small magnets of high coercivity are now produced. Magnetometric methods may become important for permanent magnets. Field strength and saturation measurements have been simplified.—J. P.

Some Special Characteristics of Soft Magnetic Materials Used in Instrument Manufacture. G. A. V. Sowter. (*Proc. Inst. Elect. Eng.*, 1951, **98,** II, Dec., 714–727). The merits of hot-rolled and-cold rolled silicon iron, 36/64 alloy, radiometal, and mumetal are outlined under a variety of conditions where high-permeability magnetic alloys are likely to be met in instrument practice. The properties found with D.C., A.C., and combined A.C.-D.C. operation, are indicated, and recommendations are made for the best alloy to be employed in particular circumstances.—H. D. W.

Single-Domain Structure in Ferromagnetic Materials and the Magnetic Properties of Finely Dispersed Substances. Part II. E. Kondorskii. (*Doklady Akademii Nauk S.S.S.R.*, 1950, **70,** 2, 215–218). [In Russian]. A summary of results obtained by calculating the distribution of magnetic moments in small isolated bodies is given, and a new estimate of the critical dimensions of single-domain particles is proposed.

Magnetostriction of Some Ferromagnetic Alloys. E. W. Lee. (*J. Iron Steel Inst.*, 1952, **171,** June, 160–164). [This issue].

Transformer Iron Losses. N. H. Crowhurst. (*Electronic Eng.*, 1951, **23,** Oct., 396–403). The design of audio-frequency transformers, compared with that of power transformers, requires more knowledge of the characteristics of the iron forming the laminations. The basic bridge circuit used for the analysis is given. Simple oscillograph patterns are shown, which form the basis of the interpretation of the results. Working details of the application and use of the charts are fully given, together with two calculated examples.—H. D. W.

The Use of Preferred Orientation Strip Steel in Turbine-Generator Stators. J. W. Apperson and C. B. Fontaine. (*Trans. Amer. Inst. Elect. Eng.*, 1951, **70,** Part I, 836–839). The paper describes the specific application of orientated 3–3½% silicon strip steel for stator punchings for turbine generators. The advantages of orientated over non-orientated strip material are discussed. A brief history of the development of the material, together with the special generator manufacturing process required when using the material, is given.—H. D. W.

The Structure of Iron–Nickel–Aluminium Alloys for Permanent Magnets. Yu. Skakov. (*Doklady Akademii Nauk S.S.S.R.*, 1951, **79,** 1, 77–80). [In Russian]. An effort to explain the problem of high coercivity of iron-nickel-aluminium alloys was made by investigating their phase composition. Metallographic analysis, measurements of physical properties, and phase analyses were made of alloys containing 33 to 70% of iron, situated in the NiAl–Fe pseudo-binary section of the Fe–Ni–Al ternary system. Direct data on the composition NiAl (β') were obtained by electrolytic separation of phases. It is concluded that the high coercivity of Fe–Ni–Al alloys is due to the formation of isolated, similarly stressed, anisotropic, dispersed inclusions of iron phase inside a weakly magnetic Ni–Al matrix.—V. G.

Magnetoscopic Checking of the Quality of Tools Made of High-Speed Steels. O. Morávek. (*Strojírenství*, 1951, **1,** Feb., 68–73). [In Czech]. The method is based on a comparison of the magnetic properties of the tool with those of a standard. If the other elements of the bridge circuit remain constant, the meter reading permits the quality of the heat-treatment of mass-produced similar parts to be instantly assessed.—E. G.

Concerning the Influence of Temperature on Magnetic Viscosity of Ferromagnetic Metals. E. F. Kuritsina. (*Doklady Akademii Nauk S.S.S.R.*, 1951, **79,** 2, 233–236). [In Russian]. The influence of temperature on the magnetic viscosity of iron and of cobalt was investigated in the ranges 86° to 1013° K. and 86° to 1073° K., respectively.—V. G.

High Frequency Permeability of Ferromagnetic Materials. R. Millership and F. V. Webster. (*Proc. Phys. Soc.*, 1950, **63B,** Oct. 1, 783–795). Methods are described for the measurement of resistive and inductive permeabilities at frequencies from 150 to 10,000 megacycles/sec. The measurements of the resistive permeabilities were carried out by comparing the alternations of a co-axial transmission line with and without the ferromagnetic as the inner conductor. The inductive permeabilities were obtained from the wavelength in a co-axial line having the ferromagnetic as the inner conductor. The results show that at all frequencies the resistive permeability is greater than the inductive, and both decrease to unity at very high frequencies.—C. J. B. F.

Magnetization Curves for Polycrystalline Ferromagnetics. H. Lawton and K. H. Stewart. (*Proc. Phys. Soc.*, 1950, **63A,** Aug. 1, 848–851). On the basis of the assumption that in polycrystalline ferromagnetic material the magnetization is approximately uniform from grain to grain, a method is developed for deriving the magnetization curves of such material by averaging the fields required to produce a given magnetization in the different constituent grains, rather than by averaging the magnetizations produced in the different grains in a given field.—C. J. B. F.

A Precise Mechanical Measurement of the Gyromagnetic Ratio of Iron. G. G. Scott. (*Physical Rev.*, 1951, **82,** May 15, 542–547). The instruments and procedure used to determine the gyromagnetic ratio of very pure iron are described. The average value obtained was $1{\cdot}0278 \pm 0{\cdot}0014$ times the mass-to-charge ratio of the electron.—R. A. R.

Iron–Silicon Alloys Heat-Treated in a Magnetic Field. Matilda Goertz. (*J. Appl. Phys.*, 1951, **22,** July, 964–965). Heat-treatment in a magnetic field is effective for Fe–Si alloys with 2–10% Si, the highest maximum permeability being obtained at about 6·5% Si. In a single crystal of this composition, magnetized parallel to a [100] direction, the hysteresis loop is squared by the magnetic anneal and the maximum permeability is increased from 50,000 to 3,800,000, the highest value yet reported.—J. P. S.

Relations between Initial and Final Orientations in Rolling and Annealing of Silicon Ferrite. B. F. Decker and D. Harker. (*J. Appl. Phys.*, 1951, **22,** July, 900–904). An investigation of the effects of rolling and annealing on the orientation of individual grains in silicon ferrite strip yielded results which have led to a theory for the appearance of the 'magnetic' orientation in the finished strip.—J. P. S.

Concerning the Nature of Elastic Anomalies of Alloys of Invar and Elinvar Types. K. P. Belov and O. N. Agasian. (*Doklady Akademii Nauk S.S.S.R.*, 1951, **80,** 6, 881–883). [In Russian]. Causes of anomalies of some Invar and Elinvar alloys (Fe–Ni; Fe–Pt; Fe–Ni–CO; Fe–Ni–Cr; and Fe–Co–Cr) with regard to volume changes with temperature and elasticity are discussed.—V. G.

Ordnance Using X-Rays to Inspect Complex Assemblies. G. Elwers. (*Iron Age*, 1951, **168,** Oct., 95–99). A betatron with platinum target developing X-rays with energies as high as 22 million electron volts is being used at the American Rock Island Arsenal to inspect complex assemblies. The high energy of this equipment allows short exposure times, the time required for a thickness of 20 in. of steel being only

20 min. Excellent detail is obtained and flaws $\frac{1}{32}$ in. deep and 0·005 to 0·002 in. wide can be detected.—A. M. F.

Radiography with Cobalt 60. A. Morrison. (*Non-Destructive Test.*, 1951, **9**, Spring, 14–22, 29). Graphs are presented from which exposure times for a range of thicknesses of steel and for different types of film can be determined when using cobalt^{60} to replace radium in industrial radiography. The physical properties of cobalt^{60} are outlined, and other information useful in handling is given. (10 references).

P. M. C.

Magnetic-Particle Crack Testing. P. Björnson, K. E. Johansson, and P. Stake. (*Jernkontorets Ann.*, 1951, **135**, 4, 129–168). [In Swedish]. Commercially available equipment and methods for the magnetic powder testing of ferromagnetic materials are surveyed.—B. S. E.

Ultrasonic Equipment for Metal Flaw Detection. (*Railway Gaz.*, 1952, **96**, Jan. 25, 94–95). In the principal locomotive and carriage works of British Railways, ultrasonic flaw detectors have become routine testing instruments. The portable apparatus, developed by Kelvin and Hughes, Ltd., will detect cracks of only molecular thickness. The principles are described.—H. F.

Ultrasonics and Their Importance in Foundry Practice. A. Vetiška. (*Hutnik*, (Prague), 1951, **1**, No. 11, 252–253). [In Czech]. Some applications and future possibilities of ultrasonics in foundry practice are discussed. The methods of Ehret and Schmid and of Sokolov for improving the structure of melts are mentioned, and the use of ultrasonics for accelerating electrolysis, and for flaw detection in castings, is cited.—P. F.

Some Applications of Ultrasonic Non-Destructive Testing. J. W. Swardt. (*J. S. African Inst. Mech. Eng.*, 1951, **1**, Oct., 51–65). The theory of ultrasonic testing is explained with its application to the detection of cracks in concrete and of flaws in machinery parts such as shafting and rails; its use for thickness measurement is indicated.—R. A. R.

Special Alloys and Electric Resistances. M. Fernier. (*Mét. Constr. Mécan.*, 1951, **83**, Nov., 863–871). The properties of alloys, mainly non-ferrous, having special expansion, electrical resistance, and magnetic properties are presented and discussed. Applications of bimetal strips and the properties of some French thermocouple alloys are dealt with.—R. A. R.

A Radial Heat Flow Apparatus for the Determination of Thermal Conductivity. A. C. Burr. (*Canad. J. Techn.*, 1951, **29**, Nov., 451–457). The apparatus described was designed for routine measurements of the thermal conductivity of materials in the range 0·001 to 0·1 c.g.s. units, but could easily be modified for measurements on metals or on refractory materials. Results are shown of the determination for the thermal conductivity of Armco iron between 400 and 700° C., together with that for electrode carbon. The accuracy is about ±5%.—B. G. B.

Creep. M. de Courcel. (*Mét. Constr. Mécan.*, 1951, **83**, Nov., 847–852). The phenomenon of creep is described in a very general way and the importance of long-time tests is stressed.—R. S.

A Survey of Recent Research on Creep of Engineering Materials. J. Marin. (*Appl. Mech. Rev.*, 1951, **4**, Dec., 633–634). A comprehensive review of the literature is presented, covering experimental studies, theoretical developments, and engineering applications. (48 references).—T. E. D.

I.C.I.'s Creep Test Research Station. E. C. Larke. (*Times Rev. Ind.*, 1952, **6**, Feb., 27–30). A complete description of the equipment is given. This includes 36 creep-testing machines, capable of exerting a force up to 5 tons. Cambridge mirror extensometers allow a 2000-fold magnification of the elongation. The laboratory is thermostatically air-conditioned, and specimens are heated in furnaces maintained within ±1° C. by platinum resistance thermometer controls. There are also 24 machines for determining the relationship between applied stress and time to rupture.—T. E. D.

Research in the Creep of Metals. (*Iron Coal Trades Rev.*, 1952, **164**, Jan. 25, 211–213). **A Creep Test Research Station.** (*Engineer*, 1952, **193**, Jan. 25, 136–137; *Engineering*, 1952, **173**, Jan. 25, 107–108). **Creep Research Station.** (*Metal Ind.*, 1952, **80**, Jan. 25, 71–72). Descriptions are given of the creep research station of Imperial Chemical Industries, Ltd., (*See* E. C. Larke, "I.C.I.'s Creep Test Research Station," the preceding abstract).

Some Factors Affecting Creep of Carbon Steel. Z. Borysowski and W. Tomaszczyk. (*Prace Głównego Instytutu Met.*, 1951, **3**, 6, 507–515). [In Polish]. The influence of chemical composition (carbon, silicon, manganese, aluminium) and other metallurgical factors (heat-treatment, grain size) on the creep strength of carbon steel is discussed.—V. G.

Investigations of the Diffusion of Iron in Four Common Iron Alloys. J. V. Garwick and I. T. Rosenqvist. (*Tidsskr. Kjemi, Bergvesen Met.*, 1951, **11**, Jan., 6–10). [In Norwegian]. The diffusibility has been determined of radioactive iron into carbon steel, cast iron, and two alloy steels, in the temperature region 600–970° C. Correlations between diffusibility and creep resistance are assumed.—B. S. E.

Steam Piping for High Pressures and High Temperatures. R. W. Bailey. (*Proc. Inst. Mech. Eng.*, 1951, **164**, 3, 324–335). The author's object is to draw attention to the more important factors which operate in piping, where, because of the temperature and stress, creep behaviour will dominate design. The following matters are considered in detail: Stresses developed as a result of creep; calculated temperature to provide for the rated temperature and pressure; the influence of creep in removing the thermal expansion loading of a pipeline at operating temperature; bolted or otherwise removable joints, especially those for joining ferritic and austenitic steel piping; and materials and corrosion.—P. M. C.

Determination of Red-Shortness in Mild Steel. J. Görrissen. (*Tidsskr. Kjemi, Bergvesen Met.*, 1949, **9**, May, 83–89). [In English]. The common methods for determination of red-shortness in mild steels are discussed.—B. S. E.

High Temperature Embrittlement in Chromium–Iron Alloys Containing 12–16% Chromium. H. Thielsch. (*Metallurgia*, 1951, **44**, Nov., 220–226). Serious embrittlement, which may be shown by ferritic stainless steels on heating at elevated temperatures, is discussed. Grain growth is not responsible, and it is suggested that embrittlement may be related to the solution of carbide. This may be prevented, or its effects overcome, by suitable heat-treatment bringing about reprecipitation of the carbides, by adjustment of composition, or by addition of carbide stabilizers.—T. E. D.

High-Nickel Alloys for Heat-Resisting Equipment. (*Henry Wiggin and Co., Ltd., publ.*, 1952). The alloys considered are Nimonic 75, essentially 80% Ni, 20% Cr; Inconel, 76% Ni, 15% Cr, balance Fe; Nimonic D, 37% Ni, 18% Cr, balance Fe; malleable nickel, 99% Ni minimum; and Mangonic, 96% Ni, 2·5–3·5% Mn. The mechanical properties of these alloys and their resistance to various atmospheres at elevated temperatures are summarized. Industrial applications and the most suitable materials for various purposes are indicated, Wire mesh conveyor belts, rollers, muffles, furnace tubes, bell furnaces, nitriding furnaces, carburizing boxes, containers, supports, thermocouple sheaths, cores, and die inserts, are quoted as examples.—T. E. D.

Periodic Checking of the Properties of Heat-Resisting Steels. E. Schwenk and A. Wüsthofen. (*BWK*, 1951, **3**, Oct., 330–331). It is suggested that all physical properties of steel used at high temperatures should be checked periodically. A programme for taking test samples after suitable periods of operation should be drawn up, appropriate spares being stocked.—E. C.

Heat-Resisting Steels for Gas Turbines and Aircraft Turbo-Engines. E. Morlet. (*Mét. Constr. Mécan.*, 1951, **83**, Nov., 915–923). The author first considers the operating conditions of the main components of gas turbines. The types of alloy used are indicated. The properties of austenitic alloys and steels are given in tables and discussed.—R. S.

Choosing The Right Low-Temperature Metals. J. R. Watt. (*Machine Design*, 1951, **23**, Oct., 117–121). Scarce materials are not necessary in all low-temperature applications. Carefully selected ordinary metals plus proper design are usually adequate. Metals whose toughness, ductility, and impact resistance increase with decreasing temperature are 'safe' at low temperatures. Such metals are aluminium, copper, nickel, and lead. The dynamics of low-temperature embrittlement, cold sensitivity in cast iron and steel, and the effect of welding are discussed.—E. C. S.

The Influence of Low-Temperature Annealing on Creep Resistance. G. Delbart and M. Ravery. (*Compt. Rend.*, 1951, **233**, Dec. 3, 1455–1457). Previous work has shown how annealing at 700° C. modifies the creep-rate/load relation. Unlike such treatment, prolonged annealing at 450° and 575° C. improves creep strength for steels of many different microstructures.—A. G.

Influence of Vacuum Fusion on the Properties of Ferrites with 25% Chromium. J. Hochmann. (*Rev. Mét.*, 1951, **48**, Oct., 734–758). These alloys exhibit brittleness particularly when the temperature of thermal treatment exceeds 950–1000° C. or after prolonged heating at 400–500° C. Vacuum fusion causes the removal of carbon, oxygen, and nitrogen, but not hydrogen, and imparts to high-chromium ferrites high strength and very high resilience. These properties are maintained after prolonged heating at 1200° C. but fall off during heating at 400–500° C. The process can be extended to iron–aluminium and iron–titanium.—A. G.

The Effects of Gases in Steels. A. Kohn. (*Mét. Constr. Mécan.*, 1951, **83,** Nov., 821–840). The article surveys the present knowledge on the solubility of gases in liquid and solid steel and on the mechanism of phenomena caused by the presence of hydrogen and nitrogen. Sections are devoted to flakes; pickling embrittlement; ageing; and steels low in phosphorus and nitrogen. (83 references).—R. S.

The Electrode-Potential Evaluation Test for Stainless Steels. C. A. Snavely, A. B. Tripler, jun., and J. H. Jackson. (*Alloy Cast. Bull.*, 1951, Mar., 3–5). This test is based on the ability of a stainless alloy to form a passive film on its surface. The electrode potential of an alloy in service may lie anwhere between that of a complete impervious film and that of the bare base metal. The test is described, and its use in research and its shortcomings are discussed.—T. E. D.

Improving Stainless Quality by the Use of Minor Selenium Additions. R. J. Wilcox. (*Alloy Cast Bull.*, 1951, Mar., 1–2). Gas porosity in low-carbon stainless castings can often be ascribed to the formation and release of hydrogen on pouring into green-sand moulds. To dry the moulds before casting is costly and inconvenient. A late addition of selenium, as ferro-selenium, will prevent the formation of internal gas voids in stainless castings of the 18/8 type; additions of as little as 0·01% of selenium to the melt are effective. Results of tests are given. The possible use of tellurium as a substitute is mentioned.—T. E. D.

Columbium and Tantalum in Austenitic Stainless Steels. J. Strauss. (*A.S.T.M. Bull.*, 1951, Oct., 17). Owing to the limited supply of niobium, recommendations have been made for modifications in the specification of niobium-stabilized steels. An appendix by H. A. Grove shows the relation between properties of present niobium steels and similar steels with a Nb : Ta ratio of approx 2 : 1.—B. G. B.

Molybdenum as Alloying Element in Constructional and Tool Steels. H. U. Meyer. (*Berg- hüttenmänn. Monatsh.*, 1951, **96,** May, 105–116). Relationships between the different mechanical properties are systematized for a number of constructional steels. It is shown that small additions of molybdenum significantly increase the hardenability, and that the element can be used economically to attain optimum mechanical properties in low-alloy steels. Molybdenum does not burn away in the melt, and its oxide is therefore suitable as an alloying addition. It eliminates or reduces temper brittleness. The question of scrap in making molybdenum-bearing steels is discussed. High-speed molybdenum steels give a performance equivalent to that of tungsten steels, but are cheaper to produce. The compositions and properties of some molybdenum tool steels are given. (20 references).—P. F.

Tool Steels from a Toolmaker's Point of View. L. Lindemann. (*Tidsskr. Kjemi, Bergvesen Met.*, 1949, **9,** May, 92–96). [In English]. The microstructural properties of typical tool steels are reviewed with regard to hardness, wear resistance, and toughness.—B. S. E.

Trends in Modern Tool Steels. C. B. Post. (*Amer. Iron Steel Inst., Preprint*, 1951). After discussing modern applications and requirements of tool steels, the author describes a classification of the various types according to their toughness, wear resistance, red hardness, and size change on hardening. The development of new types and improvements in manufacturing techniques are considered.—G. F.

Tool Steels for Hot Working. P. Henry. (*Mét. Constr. Mécan.*, 1951, **83,** Nov., 893–899). Tool steels for hot working are classified and the effects of alloying elements on their properties are stated. The characteristics of Cr, Cr–Ni–Mo, Cr–Mo, Cr–W steels and the effects of heat-treatment are reviewed.—R. S.

High-Speed Steels. A. Michel. (*Mét. Constr. Mécan.*, 1951, **83,** Nov., 873–877). The development and general properties of high-speed steels are surveyed. The three classes of high-speed steel (W 13, V 0·5%; W 18, Cr 4, V 1%; W 18, Cr 4, V 1, Co 5%) are described. Future research will cover the study of carbides, the effects of unusual elements which have produced contradictory results up to now, and the influence of angular precipitates on brittleness.—R. S.

Tools for Cold Work. L. Colombier. (*Mét. Constr. Mécan.*, 1951, **83,** Nov., 901–903). Methods for testing the quality of tools for cold work, grain-size determinations, and typical fractures are reviewed.—R. S.

The Behaviour of Zirconium and Titanium in Steels with Particular Emphasis on the Conservation of Manganese. W. W. Austin, jun. (*Amer. Iron Steel Inst., Preprint*, 1951). *See J. Iron Steel Inst.*, 1952, 170, Apr., 396.

Influence of Cobalt on the Diffusion of Carbon in Austenite. M. E. Blanter. (*Zhurnal Tekhnicheskoy Fiziki*, 1950, **20,** 1001: *Hutnické Listy*, 1951, **6,** Feb., 91). [In Czech]. The influence of cobalt on the diffusion of carbon in steel was investigated. The diffusion coefficient of carbon increases, at all carbon contents with cobalt increasing up to 6%, at temperatures up to about 1200° C., and remains unchanged with further increases in cobalt; at lower temperatures the coefficient increases up to a cobalt content of 11% and remains unchanged with higher cobalt. Many test data are presented.—E. G.

Cerium and Lanthanum Improve Hot Workability of Stainless. C. B. Post, D. G. Schoffstall, and H. O. Beaver. (*Steel*, 1951, **129,** Dec. 10, 88–91). **Rare Earths Improve Forgeability of Stainless.** C. B. Post, D. G. Schoffstall, and H. O. Beaver. (*Iron Age*, 1951, **168,** Dec. 6, 162–163). *See J. Iron Steel Inst.*, 1952, 170, Apr., 395.

Design for Steel Construction. J. N. Compton. (*Railway Steel Topics*, 1951, **1,** 1, 7–8). This is a short survey of the question of replacing castings by fabricated steel, either welded or riveted, in locomotive construction.—H. F.

Economic Utilization of Alloy Steels. F. Drastik. (*Strojirenstvi*, 1951, **1,** Apr., 125–131). [In Czech]. The measures taken in Czechoslovakia to economize in the use of alloy steels containing tungsten, chromium, nickel, and molybdenum are reviewed.—E. G.

Production of Alloy Steels. J. M. Rowland. (New Zealand Inst. Welding: *New Zealand Eng.*, 1951, **6,** Oct., 385–387). A brief description is given of the types of steel produced by an unnamed Australian company, with some relevant remarks on their production, a summary of inspection methods and standards, and the equipment in use.—P. M. C.

An Alloy Steel for Locomotive Motion Parts. J. F. Sewell. (*Railway Steel Topics*, 1951, **1,** 1, 28–32). A description of the properties of a low-alloy 0·20% C, 1·5% Mn steel containing a little nickel and molybdenum, known as 'Tormane Special,' is given. Points covered include manipulation, heat-treatment, physical properties, effect of abuse, fatigue tests, straightening, machining, and welding.—H. F.

Use of Special Steels in New Power Stations. (*Mét. Constr. Mécan.*, 1951, **83,** Nov., 905–913). Methods of determining high-temperature properties and the permissible service stresses are described. A number of French steels for valves, shafts, discs, and blades are reviewed. Future developments, and improvements in heat-treatment methods to permit of the wider use of ferritic steels, are mentioned.—R. S.

Alloy Steels in the Construction of Motor Cars. P. Sutter. (*Mét. Constr. Mécan.*, 1951, **83,** Nov., 925–927; 933). Some French standard steels for the motor-car industry and methods of classifying them are indicated.—R. S.

METALLOGRAPHY

Fractocrystallography—Method of Identification of Crystallographic Characteristics of Deformation and Fracture in Polycrystalline Solids. C. A. Zapffe and F. K. Landgraf. (*Rev. Mét.*, 1951, **48,** Nov., 811–821). The method permits the establishment of crystal models whose faces represent appropiate cleavage forms. Visual examination of plastic and elastic movement in three dimensions is made possible. Antimony and bismuth have been studied.—A. G.

An Electrical Resistance Apparatus for Studying Transformations in Metals. Its Application to Transformations in Stainless Steel. W. H. Colner and O. Zmeskal. (*Amer. Soc. Met. Preprint* 5w, 1952). The specimen, in the form of a wire, was heated by a furnace or by passing an electric current through it and quenched by cold helium. The effect of solution temperature, rate of cooling, and interrupted cooling on austenite decomposition was studied.—E. T. L.

Free Energy of Formation of Cementite and the Solubility of Cementite in Austenite. L. S. Darken and R. W. Gurry. (*Trans. Amer. Inst. Min. Met. Eng.*, 1951, 1015–1018; *J. Met.*, 1951, **3**, Nov.). The authors have computed the solubility of cementite in austenite, by thermodynamic methods, from the observed solubility of graphite. It is found that the solubility of cementite is greater than that of graphite over the entire austenite temperature range, thus partially resolving the previous discrepancy between this part of the phase diagram and the observed metastability of cementite.—G. F.

Habit Phenomenon in the Martensitic Transformation. E. S. Machlin and M. Cohen. (*Trans. Amer. Inst. Min. Met. Eng.*, 1951, 1019–1029; *J. Met.*, 1951, **3**, Nov.). The habit phenomenon in the martensitic transformation, using single crystals of a 70% Fe–30% Ni alloy, was investigated. All measured transformation strains are crystallographically equal in a given habit system, suggesting that only one reaction path operates in such a system. A series of two strains generates the correct martensitic orientation, which is consistent with the Bowles double-strain analysis for both the $\{259\}_A$ and $\{225\}_A$ habit systems. It is also shown that the Kurdjumow-Sachs orientations correspond to $\{225\}_A$ habit planes, and Greninger-Troiano orientations to $\{259\}_A$ habit planes.—G. F.

Measurement of Carbon Diffusion in Metallic Carbides. G. C. Kuczynski and R. Landauer. (*J. Appl. Phys.*, 1951, **22**, July, 952–955). A method for measuring the diffusion coefficient of carbon in metallic carbides is proposed. The rate at which excess metallic inclusions are consumed by carbon diffusing inwards from a surface is used to indicate the extent to which diffusion has taken place. Conditions are derived under which the results are susceptible to simple analytical treatment.—J. P. S.

On the General Theory of Phase Transitions. L. Tisza. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, Ltd., 1951, 1–37). A theory of phase transitions is developed from a fundamental thermodynamic relation—an expression for internal energy. The quadratic form occurring in the expansion of this function is responsible for the stability of the system being represented; if the algebraic sign of the form is indefinite, the internal energy corresponds to that at a critical point. The theory is related to various critical points of real materials, and is used to classify phase transitions.

E. T. L.

A General Method for Imperfect Crystals and Phase Transitions. J. E. Mayer. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, Ltd., 1951, 38–66). In order to facilitate the statistical-mechanical study of transitions, equations are developed for the case of imperfect crystals, by considering not single imperfect crystals but an ensemble of imperfect crystals in thermodynamic equilibrium. The average of the ensemble corresponds to a single perfect crystal, with the properties of each atom being governed by probability relations. The treatment of melting by this method is briefly discussed.—E. T. L.

Crystallization as a Co-operative Phenomenon. J. G. Kirkwood. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, Ltd., 1951, 67–76). The author points out that the task of a statistical-mechanical theory of crystallization is to describe the manner in which short-range intermolecular forces organize the long-range order of the crystal lattice. He considers the stability of a liquid phase, with respect to small perturbations of the distribution function, and takes as an example the crystallization of a system of rigid spheres. This example is further considered by O. K. Rice in the discussion.—E. T. L.

Fundamental Aspects of Diffusion in Solids. F. Seitz. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, Ltd., 1951, 77–148). The author deals with the Kirkendall effect, and outlines a simple statistical theory of diffusion and then a formal theory based on the theory of rate processes. Other sections concern the calculation of activation energies, the effect of a diffusion coefficient which depends on concentration, the effect of a vacancy current, and diffusion in metals, salts and oxides, and glasses. (39 references).—E. T. L.

Nucleation Theory. R. Smoluchowski. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948, Chapman and Hall, Ltd., 1951, 149–182). A statistical theory of nucleation is outlined in the first two sections and correlated with experimental data in the next. In the final section is a consideration of recrystallization. (40 references).—E. T. L.

Crystallographic Aspects of Phase Transformations. M. J. Buerger. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, Ltd., 1951, 183–211). The author discusses polymorphism from a thermodynamic standpoint, and divides transformations into network transformations, order transformations, transformations where the co-ordination number of the atoms is changed, and fourthly those where the bond type is altered. Examples are quoted of each, and in each the atomic motion is considered. The effect of grain size depends on the type of transformation concerned.—E. T. L.

Phase Transformations in One-Component Silicate Systems. F. C. Kracek. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, Ltd., 1951, 257–277). Hysterisis of transition is considered along with examples of both rapid and sluggish transitions, the influence of added substances called mineralizers, of temperature, crystallization, and melting. The changes of silica itself are considered in detail.—E. T. L.

Phase Transformations in Poly-Component Silicate Systems. J. F. Schairer. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, Ltd., 1951, 278–295). From a geological viewpoint the author considers melting, solid solution, and changes of crystal form and composition, dealing with incongruent melting, solid-phase stability, inversions, and unmixing. (41 references).

E. T. L.

Transformations in Pure Metals. C. S. Barrett. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, Ltd., 1951, 343–365). The author suggests a unified view of transformations in terms of dislocations, and discusses theories of shear in martensitic transformations, and the resultant crystal distortions. The lithium transformation is considered in detail, and deformation twinning is compared to strain-induced transformation. (25 references).—E. T. L.

Order–Disorder Transitions in Metal Alloys. S. Siegel. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948: Chapman and Hall, Ltd., 1951, 366–386). The concept of range of order is considered and also evidence from experiments with X-rays and on electrical, mechanical, and magnetic properties. The author then deals briefly with the kinetics of transition, and with the various theoretical approaches. In discussion, R. Smoluchowski reports that order–disorder transformation occurs by nucleation and growth, and J. E. Goldman reports a connection between magnetostriction–saturation and the degree of order in an iron–cobalt alloy.—E. T. L.

Precipitation from Solid Solutions of Metals. L. H. Geisler. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, Ltd., 1951, 387–544). This review has 830 references, and correlates the mechanism of this precipitation with the changes in properties during ageing. Ageing is attributed to the process comprising the initial formation of a transition lattice, subsequent formation of the equilibrium phase, recrystallization of the matrix, and the superimposed overall change in the composition of the matrix solid solution ion. The accelerated rates of these reactions at the grain boundaries play a prominent rôle in the interpretation of property changes.—E. T. L.

The Eutectoid Reaction. R. F. Mehl and A. Dubé. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, Ltd., 1951, 545–587). This review of the principles governing the mechanism of a eutectic transformation deals with the data on the nucleation rate and the growth rate, the interlamellar spacing in the case of pearlite, and the effect of alloying elements. The authors then consider the morphology of hypo-eutectoid steels, nucleation theory and growth theory, and the structure of bainite. (32 references).—E. T. L.

The Martensite Transformation. M. Cohen. (*Phase Transformations in Solids, Symposium at Cornell University*, Aug. 23–26, 1948; Chapman and Hall, 1951, 588–660). The features and kinetics of the martensite reaction are reviewed, with reference to the variation of the M_s temperature, the effect of continuous cooling, stabilization, and the reversal

of the transformation. A table gives the lattice relationships of various martensitic transformations, and particular attention is devoted to the shear mechanisms in steels. The author considers the thermodynamics of the transformation. (103 references).—E. T. L.

Formal Basis of Diffusion Theory. L. S. Darken. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 1–25). A survey is made of the present state of diffusion theory. The author concludes that the limited form of Fick's Law with a constant diffusivity is qualitatively or semiquantitatively fruitful for many isothermal binary or pseudo-binary systems; and the extended form of Fick's Law with a diffusivity dependent on composition is quantitatively applicable to even more binary systems, but does not give a complete description of all possible diffusion phenomena. He points out that in the general case of diffusion in multi-component systems, although general phenomenological relations are available, these are too complex to be of much practical use.—C. J. B. F.

Chemical Techniques and Analysis of Diffusion Data. C. Wells. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 26–50). The author gives details of five general methods of determining diffusion coefficients, and compares their relative merits. The evaluation and analysis of diffusion coefficient data are discussed, and a brief account of the Kirkendall technique and its recent modifications is given.

Tracer and Other Techniques of Diffusion Measurements. R. E. Hoffman. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 51–68). A critical review is made of the more widely used techniques for measuring diffusion coefficients both in alloys and pure metals. The methods chosen to be described are of general interest to practising metallurgists.—C. J. B. F.

Mechanisms of Diffusion. H. B. Huntington. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 69–86). The mechanisms of diffusion in metals are discussed in the light of the available evidence. The mechanism of interstitial diffusion in interstitial alloys is regarded as understood. For substitutional alloys three mechanisms are considered: Direct interchange, interstices, and vacancies. Theoretical studies indicate that the vacancy process is most likely in many cases.—C. J. B. F.

Diffusion in Alloys and the Kirkendall Effect. J. Bardeen and C. Herring. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 87–111). A theoretical study of the Kirkendall effect and diffusion in alloys is made from thermodynamic, phenomenological, and kinetic standpoints. A study is also made of the relationships between dislocations and the concentration of vacancies. Appendices on the relation of the diffusion coefficients for a tracer and for mass transport, and on the distribution of atoms in multi-component systems, are also given.—C. J. B. F.

Volume Diffusion—An Empirical Survey. C. E. Birchenall. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 112–128). The author makes a selective survey of the results of volume diffusion measurements, from an empirical point of view, and indicates some of the correlations that appear, also pointing out where additional data might help to settle critical theoretical questions.—C. J. B. F.

Grain Boundary and Surface Diffusion. D. Turnbull. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 129–152). In metal systems, three kinds of diffusion process are postulated, namely, lattice diffusion, grain-boundary diffusion, and surface diffusion. These are described by the diffusion coefficients D_L, D_G, and D_S, respectively. Much qualitative evidence indicates that D_G is much greater than D_L for penetration of solute atoms into a solvent metal. D_S is also much greater than D_L.—C. J. B. F.

Diffusion and High-Temperature Oxidation of Metals. C. Wagner. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 153–173). The high-temperature oxidation of metals is discussed from the standpoint of diffusion. In particular the role of lattice defects is considered, and the data available are reviewed.—C. J. B. F.

Gas–Metal Diffusion and Internal Oxidation. F. N. Rhines. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 174–191). The selectivity of gas–metal diffusion, interstitial gas–metal diffusion, the influence of structure, surface effects, and rates of gas–metal diffusion are discussed and the data reviewed. Work done on internal oxidation is also surveyed.—C. J. B. F.

Diffusion in Sintering. P. Duwez. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 192–208). Recent studies on the mechanism of sintering are reviewed. The treatment of the sintering process is divided into two parts, the first dealing with the bonding of particles (assumed to be spherical), and the second being concerned with the changes in the shapes and sizes of isolated pores. The mechanisms of these two processes are considered. The sintering of multi-component systems is discussed.—C. J. B. F.

The Migration of Grain Boundaries. J. E. Burke. (*Amer. Soc. Met. Seminar on Atom Movements*, Oct. 21–27, 1950, 209–232). Topics discussed include the driving forces for grain-boundary migration; the effects of temperature, impurities, and orientation on grain-boundary migration; and the structure of the grain boundary.—C. J. B. F.

X-Ray Investigation of the Epsilon Phase in an Fe–Mn Alloy. J. E. Parr. (*J. Iron Steel Inst.*, 1952, **171,** June, 137–141). [This issue].

The Solubility of Carbon in Molten Iron and in Iron–Silicon and Iron–Manganese Alloys. J. Chipman, R. M. Alfred, L. W. Gott, R. B. Small, D. M. Wilson, C. N. Thomson, D. L. Guernsey, and J. C. Fulton. (*Amer. Soc. Met. Preprint* 4w, 1952). The data on the solubility of carbon in iron may be expressed as a linear function of temperature between the eutectic (1153° C., 4·27% carbon) and about 2000° C. Manganese increases and silicon lessens the solubility.—E. T. L.

Gamma Loop Studies in the Iron–Titanium, Iron–Chromium, and Iron–Titanium–Chromium Systems. W. P. Roe and W. P. Fishel. (*Amer. Soc. Met. Preprint* 13w, 1952). Dilatation studies have been carried out on various alloys to determine Ac_3 transformation temperatures. These data were used to determine the shape and outer limit of the respective gamma loop curves.—E. T. L.

CORROSION

Corrosion. M. G. Fontana. (*Indust. Eng. Chem.*, 1952, **44,** Feb., 85A–88A). The corrosion data for Duriron (a 14·5% Si cast iron) are presented in condensed form. In particular, its resistance to attack by H_2SO_4 at all concentrations is stressed. The physical properties of Duriron, and methods of working it, are also listed.—C. J. B. F.

Corrosion. M. G. Fontana. (*Indust. Eng. Chem.*, 1951, **43,** Dec., 75A–78A). A review is made of a Russian paper entitled "The Effect of Acid Concentration on the Rate of Corrosion of Carbon Steels," by S. A. Balezin and T. I. Krasovitskaya. (*J. Applied Chem., U.S.S.R.*, 1951, **24,** 2, 197–202). It contains data on the corrosion in sulphuric, hydrochloric, and acetic acids of copper-bearing steels with carbon in the 0·05–0·90% range.—C. J. B. F.

The Mechanism of the Inhibition of the Corrosion of Iron by Solutions of Sodium Orthophosphate. M. J. Pryor and M. Cohen. (*J. Electrochem. Soc.*, 1951, **98,** July, 263–272). Decimolar solutions of sodium orthophosphate passivate iron at *p*H values above 7·25 in the presence of air. When the solutions are de-aerated, hydrated ferric phosphate is formed; potential–time and polarization curves indicate that the reaction is then under cathodic control. It is suggested that oxygen dissolved in the solution is mainly responsible for passivity by virtue of its heterogeneous reaction with surface iron atoms to form ferric oxide.—J. P.

Failure of a Pressure Vessel by Rapid Corrosion. D. Sandulli and E. di Giacomo. (*Calore*, 1951, **22,** Dec., 426–430). The results of tests on the remains of an exploded methane pressure vessel are described. The dangers due to impurities in the natural gas are stressed and it is shown how these were responsible for the major part of the corrosion which led to failure of the vessel.—M. D. J. B.

Contribution to the Theory of Cathodic Protection. C. Wagner. (*J. Electrochem. Soc.*, 1952, **99,** Jan., 1–12). The distribution of the electrical potential inside an electrolytic solution is calculated for typical cases of cathodic protection with the aid of an auxiliary metal to be sacrificed. These calculations are applied to work out equations and diagrams which permit prediction of the maximum extension of metallic surfaces for which cathodic protection can be accomplished.—R. A. R.

Polarization and Cathodic Protection. H. D. Holler. (*Corrosion*, 1951, **7,** Feb., 61–68). The mechanism of polarization of a galvanic couple is developed, and rôles of electrode

potentials and resistive-potential differences in polarization and cathodic protection are demonstrated. Methods of showing relations between polarizing current and galvanic-couple potential are discussed, and electrical conditions determining distribution of current flow to a galvanic couple are defined.—E. C.

Some Factors Affecting Paint Performance on Cathodically Protected Steel. A. J. Eickhoff and D. L. Hawke. (*Corrosion*, 1951, **7**, Feb., 70–74). Laboratory results on paint and cathodic protection are discussed, and effects of products of electrolysis and of electro-osmosis are described. A correlation is shown to exist between alkali resistance and cathodic protection performance.—E. C.

Combating Corrosion in a Chemical Plant with Magnesium Anodes. O. Osborn. (*Corrosion*, 1951, **7**, Jan., 2–9). The principle of corrosion protection by cathodic currents is outlined. Detailed descriptions are given of various types of galvanic anodes of magnesium and their uses in a wide range of chemical installations handling sea water at the Dow Chemical Co., Freeport, Texas. Maintenance costs are stated to have been cut to one quarter.—E. C.

Corrosion Problems in the Modern By-Product Coke Plant. C. F. Pogacar and E. A. Tice. (*Corrosion*, 1951, **7**, Mar., 76–84). Aspects of corrosion in a modern by-product coke plant are presented, and details and results of corrosion tests are quoted for test specimens and plant operation. Constructional materials for various installations are discussed in detail, and use of Monel metal and stainless steels is advocated for various units.—E. C.

Preventing Corrosion with Protective Paint Coatings. G. Diehlman and E. L. Beenfeldt. (*Corrosion*, 1951, **7**, Mar., 88–92). The efficiency of redlead as a corrosion-inhibiting pigment is emphasized. The importance of selecting suitable binding media, correct surface preparation, and proper application, is stressed. Paints and techniques for different enviromental conditions are tabulated.—E. C.

Internal and External Corrosion Experience in Shell's Products Pipe Lines. S. S. Smith, W. J. Curry, and E. H. Rush. (*Corrosion*, 1951, **7**, Jan., 20–28). Experiences with sodium nitrite as internal corrosion inhibitor in product lines are summarized. Long and short time effects of nitrite inhibition, reduction of cost, and increase in capacity are discussed. The use of magnesium anodes as an external corrosion preventive on a pipeline is described.—E. C.

Effect of Annealing on the Resistance of Galvanized Steel to Atmospheric Corrosion. S. E. Hadden. (*J. Iron Steel Inst.*, 1952, **171**, June, 121–127). [This issue].

Thermofor Catalytic Cracking Gas Plant Corrosion Survey. C. A. Murray. (*Corrosion*, 1951, **7**, Mar., 98–108). An outline is given of severe corrosion experienced in a thermophor catalytic cracking gas plant. A complete survey is made of amount and type of corrosives, principally ammonia and hydrogen sulphide, present in the gas streams, also of water present. Measures, and appropriate points, for removal of these are suggested, also points for neutralizing chemical injections to deal with remaining traces of corrosives.—E. C.

Ohio River Division Corrosion Problems. J. A. Davenport. (*Corrosion*, 1951, **7**, Feb., 42–46). Organization and duties of the Ohio River Division, Corps of Engineers, U.S. Army, are outlined. An account is given of corrosion studies on various steels and aluminium, also of tests with various coatings. The necessity for surface preparation is stressed. E. C.

Some Potential-Current Relations in Galvanic Corrosion. H. D. Holler. (*Corrosion*, 1951, **7**, Feb., 57–61). A graphical expression for electrical characteristics of a galvanic couple was developed by application of Kirchoff's laws to a couple consisting of separate electrodes with ammeters in series. Application of an external e.m.f. between the couple and a third electrode produced a definite current pattern depending on relative directions and magnitudes of applied e.m.f. and the potential of the couple. When the couple was cathodically polarized a discontinuity in potential–current relations occurred, coinciding with a zero couple current. The rise in potential results from the hydrogen over-voltage.—E. C.

Potential and Passivity. A. Ruis, and A. S. Terol. (Comité Internationale de Thermodynamique et de Cinétique Electrochimiques: *Proc. Second Meeting, Milan*, 1950, 202–204). [In French]. Anodic polarization curves of iron in N-H_2SO_4, 0·004 N-KCl are essentially the same as those in N-H_2SO_4, yet at the noble potentials where passivity usually sets in, there is still almost quantitative dissolution of iron as Fe^{++}. These results indicate that a surface film is not essential for maintaining a noble potential and that noble potentials do not necessarily signify passivity. Some revision is necessary of existing concepts relating to passivity, noble potentials, and corrosion.—J. P.

Methods of Studying Inhibitors and Stimulators of Corrosion. L. Cavallaro and A. Indelli. (Comité Internationale de Thermodynamique et de Cinétique Electrochimiques; *Proc. Second Meeting, Milan*, 1950, 205–218). [In French]. The methods by which inhibitors and stimulators have been assessed and by which their mode of action has been studied are critically reviewed. These methods include: Measurement of electrochemical potential with and without measuring the rate of corrosion; measurement of overpotential; use of macromodels of local cells; loss of weight of polarized electrodes; the pulse polarizer; and the displacement of polarization curves on applying a small external potential difference.

Notes on Corrosion and Passivation of Metals. M. Pourbaix and P. van Rysselberghe. (Comité Internationale de Thermodynamique et de Cinétique Electrochimiques: *Proc. Second Meeting, Milan*, 1950, 219–231). [In French]. A simple apparatus is described in which two samples of a metal may be polarized anodically and cathodically by the passage of a current between them and their potentials with respect to a reference electrode measured at the same time. The behaviour of Armco iron in 0·1 N-$NaHCO_3$ indicated that it will corrode in this solution only if its potential is between −0·6 and −0·39 V. with respect to the hydrogen electrode. If the potential is lower than −0·6 V. the metal is cathodically protected, hydrogen being evolved, and if above −0·39 V. it becomes passivated and covered with a protecting layer and its potential rises spontaneously to +1·1 V. In the presence of excess oxygen the potential cannot fall sufficiently low for corrosion to occur, since reduction of oxygen maintains the potential above −0·2 V. Iron is thus not corroded in oxygenated $NaHCO_3$ solution. These results are interpreted thermodynamically. Pitting will occur on differential aeration because those regions having a sufficiency of oxygen will not corrode while those without oxygen will do so. With 18: 8 Cr–Ni steel in an acetate buffer at pH 4·9, cathodic polarization by even the smallest current brings the potential below that at which hydrogen is evolved, and cathodic protection results. Similarly, even a small anodic current raises the potential above the oxygen electrode equilibrium value. This steel cannot corrode in this medium even in the absence of oxygen.—J. P.

Cathodic Current from Metal Surfaces for Determining Oxide Coatings, Adsorbed Hydrogen, and Concentration of Dissolved Oxygen, F. Tödt. (Comité Internationale de Thermodynamique et de Cinétique Electrochimiques: *Proc. Second Meeting, Milan*, 1950, 232–239). [In German]. If an unpolarizable electrode (a cadmium or iron rod in saturated $CdSO_4$, NaCl, or KCl solution) is connected to a platinum cathode immersed in an electrolyte, the internal connection being through a porous diaphragm, the current flowing in the circuit is a function of the oxygen content of the electrolyte, because the process is cathodically controlled and can proceed only as fast as dissolved oxygen can diffuse to the cathode. On connecting up the circuit after the cathode is immersed in its electrolyte, there is usually a large flow of current which eventually settles down to a low value, characteristic of the oxygen concentration of the electrolyte. This is due to there being a layer of oxygen adsorbed on the platinum, either from the air or from the solution. The amount of electricity passed until the steady state is reached is a measure of the amount of oxygen on the metal surface.—J. P.

Electrochemical Anti-Scaling Processes, M. Pourbaix and C. Rorive-Boute. (Comité Internationale de Thermodynamique et de Cinétique Electrochimiques: *Proc. Second Meeting, Milan*, 1950, 240–241). [In French]. Experiments have been carried out to determine the effect of low currents in preventing the scaling of boiler tubes. The mechanism suggested is that the metal is caused to corrode and liberate ions or colloidal products which influence the nucleation and growth of precipitated crystals, and that hydrogen peroxide formed by cathodic reduction of dissolved oxygen eventually produces hydroxyl radicals which favour chain reactions, polymerizations, and oxidations which can dislodge existing scale.—J. P.

Alcohol *vs.* Construction Materials—Stainless Steel. W. G. Renshaw. (*Chem. Eng.*, 1951, **58**, Nov., 298–300). Stainless steels are widely used in applications involving alcohol, type 304 (0·08% max. C) being the most often used. To resist methyl alcohol at high temperatures, type 316 (0·10 max. C, 16–18 Cr, 10–14 Ni, 2–3% Mo) is better than type 304.

Alcohol *vs.* Construction Materials—High-Silicon Iron. W. A. Luce. (*Chem. Eng.*, 1951, **58**, Nov., 294). High-silicon irons are unaffected in the presence of various alcohols at all temperatures and concentrations normally encountered. A high-silicon iron (Durichlor) pump used alternately for alcohol and hydrochloric acid has given many years' excellent service.

Alcohol *vs.* Construction Materials—Iron and Steel. A. W. Spitz. (*Chem. Eng.*, 1951, **58**, Nov., 297). Cast iron and steel are extensively used for tanks, pumps, and pipes conveying methyl, ethyl, butyl, and amyl alcohols, glycerine, and glycols.—R. A. R.

Chemical Plants : Protection of Steelwork. L. H. Griffiths. (*Iron Steel*, 1951, **24**, Nov., 504–506). The author discusses the protection of structural steelwork against corrosion arising out of direct contact with chemical vapours. The use of chlorinated and synthetic rubber paints is described, and the binding of steelwork with tape embedded in petroleum jelly is also mentioned.—G. F.

Corrosion of Steel in Molten Sulphur. A. Dravnieks. (*Indust. Eng. Chem.*, 1951, **43**, Dec., 2897–2900). Between 300° and 450° C., the corrosion of steel in sulphur is limited by two processes, one chemical and the other mechanical. A thin film consisting principally of ferrous sulphide grows by diffusion of reactants, presumably iron ions, through the film. The rate of corrosion is inversely proportional to the thickness of the film. With increasing thickness, mechanical strains produce film rupture followed by temporary local acceleration of attack. Kinetic constants of the reaction are given, and the film structure is described.—C. J. B. F.

The Corrosion of a Steel Surface by Condensed Films of Sulphuric Acid. D. Flint and R. W. Kear. (*J. Appl. Chem.*, 1951, **1**, Sept., 388–393). A technique for studying the corrosion of a steel surface at elevated temperatures by condensed films of sulphuric acid is described. The results were : (*a*) The rate of corrosion increases with increasing sulphuric acid dew point ; and (*b*) the rate of corrosion reaches a maximum at a surface temperature of the steel 20° to 45° C. below that of the dew point.—E. C. S.

A Standard Laboratory Corrosion Test for Metals in Phosphoric-Acid Service. H. F. Ebling and M. A. Scheil. (*Trans. Amer. Soc. Mech. Eng.*, 1951, **73**, Oct., 975–987). The authors use a standard laboratory phosphoric-acid test to evaluate materials for phosphoric-acid service. This test is critically examined. The relation between the laboratory test and the authors' field experience is presented.—D. H.

Report on Investigations into the Stress-Corrosion Cracking in Welded Gas Mains. (Brit. Weld. Res. Assoc. : *Inst. Gas Eng. Comm.*, 398, 1951). The failures generally occur between the coolers and the ammonia washers, and start inside the main. The cracks are intercrystalline and are associated with the welds. An account is given of laboratory and field tests. Stress-relieving the weldments at 450–500° C. for 1 hr. gives immunity from these failures.—B. G. B.

Research on Stainless Steels. A. Ferri. (*Met. Ital.*, 1951, **43**, Oct., 432–434). The author investigated intercrystalline corrosion cycles on three types of 18/8 austenitic steel, made suitably sensitive, in order to study the sensitivity of Strauss' test and of boiling HNO_3 tests. The results indicate that higher sensitivity can be attributed to Strauss' test—this quite apart from the well-known inhibiting action of titanium and molybdenum and the influence of heat-treatment. The scatter in the corrosion values is related to factors involved in the reactions leading to intercrystalline corrosion, *e.g.*, grain size, carbide precipitation, and surface conditions of specimens. (23 references).—M. D. J. B.

A Study of Passivity of Stainless Steel. G. P. Maitak and N. N. Gratsianskii. (*Zhurnal Prikladnoy Khimii*, 1951, **24**, 5, 545–547). [In Russian]. Reasons for the resistance to corrosion of stainless steel are discussed. The suitability of stainless steel for pickling tanks was studied. The results obtained corroborate the views expressed by Akimov.—V. G.

Corrosion and Mechanical Strength. J. B. Östby. (*Tekn. Ukeblad*, 1951, **98**, Nov. 1, 811–817). [In Norwegian]. The polarity corrosion theory is discussed and the rôle of hydrogen embrittlement is mentioned.—B. S. E.

Corrosion in Damp Conditions. A. J. Maurin. (*Electrotechnique*, 1951, Reprint). The application of thermodynamics and the use of the Fe–H_2O equilibrium diagram to combat corrosion is explained. The protection of the hulls of ships by zinc strips, and of gasholders and water tanks by magnesium, is shown. Some of the many special methods of protection designed for underground pipelines are described with illustrations. The theoretical calculations required for the latter are explained.—B. G. B.

Welding Unstabilized Austenitic Stainless Steels without Carbide Precipitation. J. A. Goodford, and D. W. Kaufmann. (*Mat. Methods*, 1951, **34**, Nov., 64, 65). The authors claim that rapid cooling of the heat-affected zone promptly after welding reduces the chances of subsequent intergranular corrosion. Water, applied by hose or swab, may be used to reduce the temperature of the weld metal to below 800° F. in under 2 min. This treatment greatly retards chromium carbide precipitation.

ANALYSIS

The Use of the Spekker Photoelectric Absorptiometer for Precision Measurements. F. F. Pollak and J. W. Nicholas. (*Metallurgia*, 1951, **44**, Dec., 319–326). An account is given of the H6O2 Spekker absorptiometer with mercury vapour lamp. The technique of its use is discussed. The use and preparation of monochromatic filters, the recalibration of the drum scale in true density, and the determination of the true optical depth of glass cells are described. The extension of the scale for measurement of high densities, by the use of neutral filters, is also dealt with. (35 references).—B. G. B.

Spectrographic Analysis of Cast Irons. M. Scalise. (*Met. Ital.*, 1951, **43**, Nov., 471–475). The author describes the results of tests on a method of quantitative spectrographic analysis for cast irons. A medium-dispersion prism spectrograph was used. The author stresses the economic advantages of this method compared with chemical methods.
M. D. J. B.

Spectrophotometric Analysis and Its Application to Ferrous Metallurgical Analysis. M. Jean. (*Anal. Chim. Acta.*, 1952, **6**, Feb., 157–185). [In French]. A spectrophotometer for colorimetric analysis with monochromatic light is described and illustrated. Operating details, with typical calibration graphs and discussion of previously published information, are given for the determination of the following elements : manganese, silicon, phosphorus, copper, nickel, chromium, molybdenum, tungsten, cobalt, titanium, vanadium, and lead.
J. O. L.

Determination of Chromium, Vanadium and Molybdenum by the Use of Radioactive Tracers. J. Govaerts and C. Barcia-Goyanes. (*Anal. Chim. Acta*, 1952, **6**, Feb., 121–125). [In French]. Using radioactive silver as a solution of its nitrate, precipitates of silver chromate, vanadate, and molybdate can be obtained under standardized conditions and their activities measured by a Geiger-Müller counter. Comparison with curves prepared from solutions containing known concentrations enable the elements chromium, vanadium, and molybdenum to be determined over a wide range with an accuracy greater than that usually achieved by chemical methods.—J. O. L.

The Colorimetric Determination of Titanium in Steels in the Presence of Vanadium, Using Chromotropic Acid. R. Rosotte and E. Jaudon. (*Anal. Chim. Acta*, 1952, **6**, Feb., 149–156). [In French]. After removal of iron by mercury cathode electrolysis, titanium can be determined in steels by measurement of the colour of its complex with chromotropic acid at 460 mμ. The colour is shown to be stable over a long period and to be independent of the vanadium concentration. The effect of temperature, *p*H, and composition of solution have been studied and a suitable method of operation is described.—J. O. L.

Determination of Sulphate in Chromium Baths Using Radiobarium. S. L. Eisler. (*Metal Finishing*, 1952, **50**, Jan., 71–74). Sulphate is determined by reducing the chromic acid and adding slight excess barium chloride solution containing radiobarium. The solution is filtered and an aliquot portion of the filtrate is evaporated to dryness and counted. The sulphate content of the original sample is inversely proportional to the counting rate. The results are compared with those obtained gravimetrically ; the radiochemical method is more accurate.—J. P.

Polarographic Examination of Some Amino-Acid Complexes Formed with Ferrous Metals. R. Pleticha. (*Chem. Listy*, 1951, **45,** May, 185–189). [In Czech]. A description is given of a polarographic and oscillographic study of complexes of amino acids formed with ferrous metals, and of their stability.—P. F.

Microchemical Test for Divalent Iron By Isonitrosodibenzoylmethane. F. Vlačil and V. Hovorka. (*Chem. Listy*, 1951, **45,** Oct., 439–442). [In Czech]. It was found that the formation of a coloured inner complex in the reaction of divalent iron with an alcoholic solution of isonitrosodibenzoylmethane provided the most sensitive of the ' iron blue reactions ' used for the microchemical detection of ferrous ions. The use and sensitivity of the method are discussed and its scope and modifications necessary in the presence of certain other ions are given. The reagent is inapplicable if nickel and cobalt are present, as these also form coloured complexes with it.—P. F.

A New Method of Gas Analysis. W. B. Bartley. (*Coke Gas*, 1952, **14,** Jan., 30–32). The principle of the infra-red absorption method for the continuous analysis of gases is described. Particular reference is made to the Infra-Red Development Co. equipment for the analysis of CH_4, CO, and CO_2 in flue gases, coke-oven gas, and blast-furnace gas. T. E. D.

HISTORICAL

Rolling of Round Iron Bars at the Beginning of the XVIIth Century. R. Herwig. (*Stahl u. Eisen*, 1951 **71,** Dec. 6, 1397–1398). Documentary evidence is produced for the existence, during the first decade of the XVIIth century, of mills for rolling round iron bars from square billets.—J. P.

Andrew Yarranton and the Saxon Tinplate Industry. E. Matthes. (*Stahl u. Eisen*, 1951, **71,** Dec. 20, 1444). The book " England's Improvement by Sea and Land " by Yarranton himself is quoted to show that when he went to Saxony to investigate the tinplate industry there, he and his companion were received hospitably and did not resort to disguise in order to ' spy.'—J. P.

Iron and Steel Wire Drawing about 1700 in the Lower Dill Valley. R. Herwig. (*Stahl u. Eisen*, 1952, **72,** Jan. 17, 53–57). A wire-drawing shop existed in Asslar about 1700 and had a staff of more than 20. Working conditions, equipment, and costs, as revealed by ancient documents, are discussed.—J. P.

Excerpts from Correspondence of a 19th-Century Ironfounder. T. R. Harris. (*Foundry Trade J.*, 1952, **92,** Jan. 24, 99–101). Extracts from the letter books of a Cornish ironfounder throw light on employment conditions, cupola melting, moulding sand, prices, making large castings and cylinders, complaints, and designs.—E. T. L.

ECONOMICS AND STATISTICS

Vertical Interrelation in the Iron and Steel Industries in the United States of America and Great Britain. W. Lauersen. (*Stahl u. Eisen*, 1952, **72,** Jan. 31, 109–117). The amalgamation of coal and ore mining, the production of iron, steel, and semi-finished materials, and various forms of engineering, into financial groupings in the U.S.A. and in Great Britain, are discussed.

Research, Technology, and Economics In Steel Development. E. H. Schulz. (*Berg- hüttenmänn. Monatsh.*, 1951, **96,** Dec., 241–246). The author, pointing to the controlling influence of economic criteria operating through the medium of production upon trends in research, concludes that from a long-term viewpoint expenditure on research, not least fundamental research, is a good investment even if results are not immediate ; that it should be the task of research workers to search for ways of applying results of basic research in technology ; that a simple and concise presentation of technical and scientific data is imperative ; that research workers should strive not only to deepen but also to broaden their knowledge beyond their immediate problems so as to be able to discover new applications of results in technology ; and that team-work not only between scientists but between scientists and technologists, in, and between, steelmaking and steel-shaping branches of the industry is desirable.—P. F.

Achievements and Advances in the Metallurgy of Iron and Steel. R. Graef. (*Stahl u. Eisen*, 1952, **72,** Jan. 3, 1–10). The differences between the outputs of American and European iron and steel industries are considered in relation to the European shortage of fuel and high-grade ores. It is concluded that mass production and changed working conditions can lead to outputs per man in European steelwork and rolling mills as high as those in America, in spite of the lack of capital.—J. P.

Principles of Budget Cost Accounting and Its Application to the Special Steels Industry. W. Rocker. (*Stahl u. Eisen*, 1952, **72,** Jan. 31, 134–142). Various methods of cost accounting are reviewed and a comprehensive explanation is given of the concepts behind them. The preparation, carrying out, and evaluation of the standard cost accounting for a producer of special steels are described and illustrated by examples.

The Iron Age 1952 Metal Industry Facts. (Iron Age, 1952, **169,** Jan. 3, 381–476). These pages consist of tables relating to production, markets, and prices in the American metal industries. They are presented in eight sections : (1) Steel industry ; (2) non-ferrous metals ; (3) raw materials ; (4) metal products ; (5) casting and forging ; (6) machinery ; (7) market data ; and (8) labour and safety.—R. A. R.

MISCELLANEOUS

Human Relations in the Open Hearth. R. Smith. (*Amer. Iron Steel Inst.*, 1951, *Preprint*).

Silence Is Not Always Golden. H. B. Jordan. (*Amer. Iron Steel Inst.*, 1951, *Preprint*). The author discusses the apparent gradual deterioration in public understanding of business and industry, particularly of the iron and steel industry, and analyses the problem.—G. F.

A Program of Community Economic Education. J. M. Underwood. (*Amer. Iron Steel Inst.*, 1951, *Preprint*).

The Making of Technical Men for Industry. F. C. Lindvall. (*Amer. Iron Steel Inst.*, 1951, *Preprint*).

Education, Research and the Steel Industry. H. T. Heald. (*Amer. Iron Steel Inst.*, 1951, *Preprint*).

BOOK NOTICES

Borchers, Heinz. " *Metallkunde.*" Zweite Auflage. Small 8vo. Illustrated. " *I. Aufbau der Metalle und Legierungen,*" pp. 110. " *II. Eigenschaften. Grundsätze der Form- und Zustandsgebung,*" pp. 154. Berlin, 1950, 1951 : Walter Gruyter & Co. (Price DM 2.40 per volume).

These two pocket-sized booklets are Nos. 432 and 433 in the extensive " Sammlung Göschen " publications, which embrace practically all branches of technology and many branches of the liberal arts, history, languages, etc. Just over 100 and 150 pages long, respectively, they are more-or-less a ' digest ' of information, and inevitably suffer from the defects inherent in this type of literature, but within their limitations of size and scope they do give the reader a reasonably thorough and very readable account of physical metallurgy for engineers.

Volume I covers the subjects of the crystalline structure and nature of single-phase metals and polyphase systems of alloys, explains clearly and simply the meaning of an equilibrium diagram, and gives numerous examples of the diagrams of the commoner alloys. The drawings and microphotographs are, of course, small, but are remarkably clear nevertheless. No attempt is made, however, to treat the subject from a fundamental standpoint ; in fact, the Phase Rule is considered only very briefly and at the very end of the book.

Volume II shortly recapitulates the subjects of metals and alloys, with particular regard to the physical properties and how these are affected by temperature, composition, etc. The main part of the book is devoted to an account of the general ways of dealing with metals, again from an engineer's viewpoint more than any other ; casting, spraying, sintering of powder, heat-treatment, forging, cutting, and machining, are all considered briefly.

The illustrations and diagrams are good, and each volume contains an index and a short bibliography. For the man who is not essentially a metallurgist but who wishes to know something of the scope and nature of metallurgy, these books are excellently designed.—D. J. C. Brandt

BOUSSARD, FRANÇOIS. "Défauts de Fonderie," Préface du Professeur Albert Portevin. 8vo, pp. viii + 424. Illustrated. Paris, 1952 : Dunod. (Price 2700 fr.)

This work is the outcome of a survey of casting defects undertaken by the Technical Committee of the Belgian Foundry Association, following a suggestion made by Professor Portevin at the 1938 International Foundry Congress. The author is a former student of the École Supérieure de Fonderie, and these published findings which are the result of an interchange of information between numerous foundrymen over a long period, have been submitted to the scrutiny of the Technical Committee.

Apart from a brief introduction, the body of the work is devoted to a systematic presentation of defects, grouped broadly according to type : Faults due to shrinkage and contraction ; defects deriving from the casting properties of the material, from lack of uniformity in composition and structure, from inclusions, gases, and moulding materials ; and, finally, defects due to the pressure of metal in the mould and those arising from faulty patterns or badly designed moulds and cores. For each of the 72 defects there is a definition which is followed by notes on the mechanism of its formation, its appearance and cause, and the appropriate remedies.

The two closing chapters consist of tabulated data based on the foregoing. In the first, defects are classified according to their physical characteristics ; in the second (presumably for the use of students and apprentices), the recommended precautions are recapitulated, with the defects to which they refer in an adjoining column.

Comparison with similar publications issued by the Institute of British Foundrymen and the American Foundrymen's Society suggests that a future edition of this book would benefit by the substitution of photographs for the somewhat over-simplified diagrams at present used. The work, however, presents the first logical approach to the subject in French ; the general review of the fundamental principles involved, which appears at the beginning of each group of defects studied, is to be commended. In passing, it may be questioned whether the author's explanation that the 'eggshell' defect (*coquille d'œuf*) is due to entrained air in the mould is the correct one. Professor Hénon has advanced a somewhat different explanation for this phenomenon.—G. R. WOODWARD

FUCHS, R., and H. BRADLEY. "*Welding Practice.*" Vol. I. "*Welding Methods and Tests.*" La. 8vo, pp. xii + 130. Illustrated. London, 1951 : Butterworth's Scientific Publications, Ltd. (Price 17*s.* 6*d.*)

This volume, which is complementary to two others under the same general heading, deals authoritatively with the practical aspects of welding as seen through the eyes of one of the largest industrial users of welding in the country. The information that it contains was orginally prepared for internal use as a series of separate booklets by some of the leading technical experts of Imperial Chemical Industries, Ltd.

The object of the book is not to deal generally or comprehensively in textbook form with welding, but rather to meet the practical welding needs of designers, draughtsmen, engineers, and foremen. This has been done in a very clear and concise manner, treating established fundamentals selectively and briefly, and elaborating rather more on recently established or lesser-known facts. Five main subjects are covered, namely, welding processes, welding metallurgy, weld examination and testing, welding equipment and shop layout, and welfare and safety in the practice of welding.

The first chapter deals with each of the main welding processes in an effort to define their best fields of application, and even if there is a tendency to sacrifice accuracy in places, this is obviously due to the demands of brevity. Argonarc welding is disposed of in less than a page, which is hardly adequate for a new and important process that is finding a rapidly increasing field of application in the welding of aluminium and its alloys, copper and its alloys, and corrosion- and heat-resisting steels.

Chapter 2 gives a really easily digestible treatment of those metallurgical features which influence the welding operation. Metallurgy is a subject which often alarms the engineer, but the language used here is so simple as to arouse his interest ; a particularly useful section deals with the impurities in metals, and discriminates between the harmful ones and those which can actually be beneficial in welding.

Non-destructive and destructive tests are covered in Chapter 3, with emphasis on radiography, and attention is drawn to the usefulness of ordinary visual examination if it is intelligently carried out. The important destructive testing methods are discussed clearly and critically, detailing particularly the relatively standardized methods.

Questions of welding equipment and shop layout (Chapter 4) are covered in a way which reflects the admirable practical outlook of the apparently academic list of authors. A narrow trolley for oxy-acetylene equipment is shown in one of the many excellent illustrations, and whilst the advantage of this is obvious from the photograph, it is probable that this has not yet been widely recognized.

Chapter 5 deals in an unusually clear and comprehensive manner with welfare and safety in welding, drawing special attention to the precautions required in the repair by welding of containers of inflammable liquids. A glossary of terms and a four-page index complete a volume which will be indispensable to those connected with the practice of welding.—A. J. HIPPERSON

LUMSDEN, JOHN. "*Thermodynamics of Alloys.*" Institute of Metals Monograph and Report Series No. 11. 8vo, pp. xv + 384. Illustrated. London, 1952 : The Institute. (Price 35*s.*)

Mr. Lumsden has written an excellent book, which should be read by everyone interested in the physical chemistry of metals ; it should appeal in particular to senior students and research workers. The book reflects the metallurgical interests of the Imperial Smelting Corporation, but that is no shortcoming. It has obviously been put together with great care and thoroughness ; it is pleasant to read, never tedious, and has been well printed and well bound. The reader should be familiar with differential and integral calculus, and also have an elementary knowledge of classical thermodynamics. Although the laws of thermodynamics, and the conclusions drawn from them, are based on first principles, they are developed mathematically. The uninitiated reader will find it very difficult to follow them,

The book opens with a chapter on mathematics, in which is included an account of partial differentiation, and a description of the relationship between thermodynamics and statistical mechanics. There follows a chapter on the degradation of energy, in which the first and second laws of thermodynamics are discussed, and the incomplete availability of heat as a source of work is attributed to the randomness of the thermal motions of atoms and molecules. The randomness of distribution of the momenta and locations of atoms and molecules are then considered on a statistical basis, and are linked with the equi-partition of kinetic energy and the definition of temperature. The concepts of entropy and free energy are then developed in terms of randomness, and their application to homogeneous and heterogeneous equilibria is discussed.

After a chapter on the quantization of energy, consideration is given to the heat capacities, thermal expansions, and entropies of solid and liquid metals—these properties being considered in terms of the vibration spectra of the metal atoms. A chapter on imperfect gases leads to a treatment of the vapour pressures of metals, in which the available data on cadmium, zinc, magnesium, lead, and bismuth are critically reviewed, and summarized in appropriate equations.

The second half of the book is devoted to binary alloy solutions, which are excellently treated. Heats of mixing and free-energy curves, and the corresponding partial molal quantities, are described, with examples from the zinc–cadmium, zinc–tin, and mercury–bismuth systems. The laws of very dilute and moderately dilute solutions are developed statistically, the relation between entropy and the distribution of solvent and solute atoms being clearly described. No reference is made to ternary solutions.

There follows a description of the manner in which different types of physico-chemical measurements in liquid alloys can be correlated to give a complete description of the thermodynamic properties of these alloys. The zinc–

tin and zinc–cadmium systems are taken as examples, the available data on each being treated critically and in full detail. Heats of fusion and the theory of freezing-point depressions are next described, with the examples of cadmium, lead, thallium, tin, bismuth, and silver.

A detailed study of the zinc–copper system is used to illustrate the application of thermodynamic calculations to complex binary systems. This is followed by a chapter on the free energy of liquid alloys, with detailed discussion of the systems lead–bismuth, potassium–mercury, cadmium–lead, thallium–bismuth, thallium–mercury, bismuth–mercury, silver–gold, zinc–cadmium, and thallium–lead.

The last few chapters deal with the statistical mechanics of solid and liquid solutions, and include statistical treatments of the energies and entropies of mixing, and the calculation of ' thermal ' entropies from vibration frequencies in solid solutions. There is an interesting section on regular behaviour, which draws attention to the fact that regularity (*i.e.*, ideal entropies of mixing) implies not only that the distribution of the molecular or atomic species in a binary solution is uniform, but also that the ' thermal ' entropy is not influenced by mixing. As the latter proviso is not likely to be generally true, regular behaviour must be the exception rather than the rule.

The book is characterized by clarity of thought and expression, and by the carefully considered examples of metal and alloy behaviour which it contains. It is free from that vagueness and superficiality which is so commonly found in writings on thermodynamics. The reader will find the book of great value, whether he regards thermodynamics merely as a means of making the most of the data available on metal systems, or whether he is interested in the linking of the atomic structures of alloys with their thermodynamic properties *via* statistical mechanics.

F. D. RICHARDSON

MILLS, E. D. " *The Modern Factory.*" 4to, pp. 190. Illustrated. London, 1951: Architectural Press, Ltd. (Price 30*s.*)

At some stage in their careers most successful architects and engineers feel the urge to write a technical book. Although only a small proportion ever gets into print, the number of new books which appear every year is surprisingly high. Many of them have a fairly general appeal—they are not for the scholar, nor for the specialist; they are intended for the liberally minded top-ranking executive and appeal to the technically inclined dilettante.

" The Modern Factory " is too superficial for students and the subject matter too well known for the professional architect. It may be useful, however, to show management the contrast between the sort of factory buildings which can be erected today and the familiar blots on the landscape of our industrial areas.

The author has a considerable amount of interesting and valuable information to impart. The fundamentals of factory layout and design are given. Functional requirements of a wide variety of industrial buildings are discussed, and the manner in which these can best be met is the real subject of the book.

It is perhaps a pity that the writing of a book treating of architecture should be so deficient in style. The illustrations, however, are excellent, particularly the photographs, which give a selection of buildings especially chosen to illustrate the points made in the book. Examples are given of factories, laboratories, warehouses, offices, canteens, and welfare buildings constructed in the United Kingdom, Ireland, the U.S.A., Switzerland, Sweden, Holland, South Africa, and Italy.—M. D. J. BRISBY

SOCIETY OF GLASS TECHNOLOGY. " *Directory for the British Glass Industry*, 1951." 8vo, pp. 415. Sheffield, 1952: The Society of Glass Technology. (Price 12*s.* 6*d.*)

This publication lists glass manufacturers, glass fabricators, and the manufacturers of scientific, optical, constructional, and decorative glass, and the suppliers of glass-making plant, machinery, and materials. The industrial associations, trade unions, research organizations and technical societies dealing with glass, as well as the educational institutions giving courses on some aspect of glass-making or treatment, are also listed. This volume should be widely used in the glass industry, and will be of considerable assistance to those requiring special optical and chemical glassware.—J. P. S.

SOCIETY OF GLASS TECHNOLOGY. " *Glass and W. E. S. Turner*, 1915–1951." Edited by F. T. Gooding and E. Meigh. 4to, pp. 144. Sheffield, 1951: The Society. (Price 20*s.*)

Dr. W. E. S. Turner, whose seventieth birthday is commemorated by this book, was the first Head of the Department of Glass Technology at Sheffield University and the Founder of the Society of Glass Technology. When he ' invaded ' the industry—so the editors describe his first contact—operations were a matter of rule-of-thumb, and composition and processes were well-kept secrets. The War of 1914–18, however, found Britain short of chemical and optical glassware, and the need for rapid and scientific study of the production of these qualities of glass opened a door through which scientific method, pioneered by Dr. Turner, entered to revolutionize the industry. From the first establishment of the Society of Glass Technology, manufacturers, managers, and foremen came together to read and discuss papers and soon to discuss their own problems with freedom and candour. This new interchange of information found response all over the world, and similar societies came into existence in most industrial countries, parallel with the renewed world-wide interest in the technology of glass. In this development, as in the raising of British levels of understanding and research, Dr. Turner was an outstanding leader. A large part of this book deals with the growth of knowledge, over the last 35 years, of glass chemistry, of the melting process, and of glass-making refractories, and evidence of the effect of Dr. Turner's work, and of the work of the Society, are to be traced on almost every page. The same is true of production, which has passed extremely rapidly from laborious hand methods to the use of large, ingenious machinery. Nor has the Society's influence on decorative glassware been insignificant. Dr. Turner himself addressed the First Glass Convention in 1928 on " Modern Art Glass " and, later, made a collection of the works of modern artists in glass, which he presented to his Department. There may be little in this book of direct interest to the metallurgist or to the refractory chemist, but it abounds with examples of the way in which the application of science galvanized a moribund industry into a new and fuller life.—J. P. S.

NEW PUBLICATIONS

AMERICAN IRON AND STEEL INSTITUTE and AMERICAN CERAMICS SOCIETY. " *Refractories Bibliography*, 1928–1947 *Inclusive.*" La. 4to, pp. iv + 1087. Columbus, Ohio, 1950: American Ceramic Society, Inc. (Price $15)

AMERICAN SOCIETY FOR TESTING MATERIALS. " 1951 *Supplement to the Book of ASTM Standards.*" 8vo, illustrated. " *Part I.—Ferrous Metals,*" pp. xi + 401. " *Part* 2.—*Non-Ferrous Metals,*" pp. xi + 345. " *Part* 3.—*Cement, Concrete, Ceramics, Thermal Insulation, Road Materials, Waterproofing, Soils,*" pp. xiii + 265. " *Part* 4.—*Paint, Naval Stores, Wood, Adhesives, Paper, Shipping Containers,*" pp. xiii + 249. " *Part* 5.—*Textiles, Soap, Fuels, Petroleum, Aromatic Hydrocarbons, Antifreezes, Water,* pp. xiii + 320. " *Part* 6.—*Electrical Insulation, Plastics, Rubber,*" pp. xiii + 233. Philadelphia, Pa., 1951: The Society. (Price $21 for 6 parts)

ASSOCIATION TECHNIQUE DE FONDERIE DE BELGIQUE. " *Mémoires du Congrès International du Fonderie, Bruxelles*, 1951." La. 8vo, pp. xlvii + 516. Illustrated. Brussels, 1951: The Association. (Price 72*s.*)

ASTBURY, N. F. " *Industrial Magnetic Testing.*" 8vo, pp. 132. Illustrated. Physics in Industry. London, 1952: The Institute of Physics. (Price 25*s.*)

AZIENDA MINERALI METALLICI ITALIANI. " *Metalli Non-Ferrosi e Ferroleghi*; *Statistiche* 1950." " Non-Ferrous Metals and Ferro-Alloys; Statistics 1950." 4to, pp. xxiii + 155. Rome, 1950: Azienda Minerali Metallici Italiani.

BEGEMAN, MYRON L. "*Manufacturing Processes.*" 3rd ed. 8vo, pp. 608. Illustrated. New York: John Wiley and Sons, Inc. (Price $6)

BRITISH STANDARDS INSTITUTION. B.S. 499: 1952. Section 7. "*Scheme of Symbols for Welding.*" 8vo, pp. 47. Illustrated. London, 1952: The Institution. (Price 6*s.*)

BRITISH STANDARDS INSTITUTION. B.S. 639: 1952. "*Covered Electrodes for the Metal-Arc Welding of Mild Steel (12 S.W.G. ($\frac{3}{32}$ in.) and larger, for hand operation).*" 8vo, pp. 33. Illustrated. London, 1952: The Institution. (Price 4*s.*)

BRITISH STANDARDS INSTITUTION. B.S. 1756: 1952. "*Code for the Sampling and Analysis of Flue Gases.*" 8vo, pp. 78. Illustrated. London, 1952: The Institution. (Price 10*s.* 6*d.*)

BRITISH STANDARDS INSTITUTION. B.S. 1796: 1952. "*Methods for the Use of B.S. Fine-Mesh Test Sieves.*" 8vo, pp. 27. Illustrated. London, 1952: The Institution. (Price 3*s.* 6*d.*)

BRITISH STANDARDS INSTITUTION. B.S. 1797: 1952. "*Tables for Use in the Calibration of Volumetric Glassware.*" 8vo, pp. 87. London, 1952: The Institution. (Price 10*s.* 6*d.*)

BRITISH STANDARDS INSTITUTION. B.S. 1816: 1952. "*Heavy Duty Cooking Ranges (Solid Fuel).*" 8vo, pp. 20. Illustrated. London, 1952: The Institution. (Price 3*s.*)

BRITISH STANDARDS INSTITUTION. B.S. 1821: 1952. "*Oxy-Acetylene Welding of High Temperature & High Pressure Pipelines.*" 8vo, pp. 51. Illustrated. London, 1952: The Institution. (Price 6*s.*)

BRITISH STANDARDS INSTITUTION. B.S. 1822: 1952. "*Nickel Clad Steel.*" 8vo, pp. 9. London, 1952: The Institution. (Price 2*s.*)

BRITISH STANDARDS INSTITUTION. B.S. 1823: 1952. "*Stainless Steel Hollow-ware for Use in Hospital Operating-Theatres & Wards.*" 8vo, pp. 15. Illustrated. London, 1952: The Institution. (Price 2*s.*)

BRITISH STANDARDS INSTITUTION. B.S. 1840: 1952. "*Tubular Steel Columns for Street Lighting.*" 8vo, pp. 23. Illustrated. London, 1952: The Institution. (Price 3*s.*)

BRITISH STANDARDS INSTITUTION. B.S. 1843: 1952. "*Colour Code for Twin Compensating Cables for Thermo-couples.*" 8vo, pp. 6. London, 1952: The Institution. (Price 1*s.*)

CAMPBELL, CHARLES H. "*Modern Pyrometry.*" 8vo, pp. 150. Illustrated. 1951: Chemical Publishing Co., Inc. (Price $4)

"*Case Study Data on Productivity and Factory Performance—Gray Iron Foundries.*" Published by the United States Department of Labour. Pp. 104. London, 1951: British Institute of Management. (Price 20*s.*)

CHESTNUT, H., and R. W. MEYER. "*Servomechanisms and Regulating System Design.*" Vol. I, pp. xi + 505. Illustrated. New York, 1951: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd. (Price 62*s.*)

COPPER DEVELOPMENT ASSOCIATION. "*The Welding, Brazing and Soldering of Copper and its Alloys.*" C.D.A. Publication No. 47, 1951. 8vo, pp. 188. Illustrated. Radlett, Herts., 1951: The Association.

DAVIES, T. H. "*Telford Clarence Batchelor (1857–1947).*" A Memoir describing his Invention and Development of Locked-Coil and Flattened-Strand Wire Ropes, with a Foreword by H. W. Dickinson. La. 4to, pp. x + 69. Illustrated. London, 1951: Courier Press.

"*Directory for the British Glass Industry.*" 5th ed. Compiled by D. W. Rollin and E. Rollin. 8vo, pp. 415. Sheffield, 1951: Society of Glass Technology. (Price 12*s.* 6*d.*)

EDWARDS, W. "*The Concealed Coalfield of Yorkshire and Nottinghamshire.*" Third Edition. Department of Scientific and Industrial Research, Memoirs of the Geological Survey, England and Wales. 8vo, pp. x + 285. London, 1951: H.M. Stationery Office. (Price 22*s.* 6*d.*)

EISENKOLB, FRITZ. "*Das Tiefziehblech.*" Herausgegeben von Dipl.-Ing. Werner Engelhardt. 8vo, pp. xii + 363. Illustrated. Leipzig, 1951: Akademische Verlagsgesellschaft Geest u. Portig K.-G. (Price 50*s.*)

FARRINGTON, G. H. "*Fundamentals of Automatic Control.*" Pp. xii + 285. Illustrated. London, 1951: Chapman and Hall, Ltd. (Price 30*s.*)

GELEJI, ALEXANDER. "*Die Berechnung der Kräfte und des Kraftbedarfs bei der Formgebung im bildsamen Zustande der Metalle.*" 8vo, pp. 248. Illustrated. Budapest, 1952: Akademiai Kiado.

HENNING, F. "*Temperaturmessung.*" Pp. 294. Illustrated. Leipzig, 1951: Johann Ambrosius Barth. (Price DM 26.80)

JEFFERSON, T. B. "*The Welding Encyclopedia.*" 13th ed. Pp. 1008. New York, 1951: McGraw-Hill Book Co.

KENNEL, ERNST. "*Das Nieten im Stahl- und Leichtmetallbau.*" 8vo, pp. 190. Illustrated. München, 1951: Carl Hanser Verlag.

KLOSTERMANN, PAUL. "*Die Praxis der Warmbehandlung des Stahles.*" 6. verb. Aufl. 8vo, pp. 68. Illustrated. (Werkstattbücher für Betriebsangestellte, Konstrukteure und Facharbeiter, H.8). Berlin, Göttingen, Heidelberg, 1952: Springer-Verlag. (Price DM 3.60)

KOCH, J. J., R. G. BOITEN, A. L. BIERMASZ, G. P. ROSZBACH and G. W. VAN SANTEN. "*Strain Gauges, Theory and Application.*" Philips Technical Library. 8vo, pp. viii + 95. Illustrated. Eindhoven, Holland, 1952: N.V. Philips' Gloeilampenfabrieken; London: Cleaver Hume Press, Ltd. (Price 15*s.*)

LAQUE, FRANCIS L. "*Corrosion Testing.*" Edgar Marburg Lecture, 1951. 8vo, pp. 89. Illustrated. Philadelphia, Pa., 1951: American Society for Testing Materials. (Price $1.50)

MCGERRIGLE, H. W., and H. GIRARD. "*Les gites de fer de la Province de Québec.*" La. 4to, pp. 50. Quebec, Canada: Ministère des Mines de la Province de Québec.

MEINCK, F., P. SANDER, H. STOOFF, and R. WELDERT. "*Industrie-Abwässer,*" mit einem klärtechnischen Teil von H. Kohlschütter. Schriftenreihe des Vereins für Wasser-, Boden- und Lufthygiene, Berlin-Dahlem, Nr. 6, Lfg. 1, Bg. 1 bis 4. Pp. 64. Illustrated. Stuttgart, 1951: Piscator-Verlag. (Price DM 8.– An order for Lfg. 1 renders purchase of all other parts obligatory)

"*100 Jahre Niederrheinische Hütte Aktiengesellschaft, Duisburg, 1851–1951.*" Bearb.: Professor Dr.-Ing. Max Paschke, Dr. Hugo Racine, Professor Dr.-Ing. Ernst Hermann Schulz u. Gert von Klass. 4to, pp. 89. Illustrated. Darmstadt, 1951: Verlag Hoppenstedts Wirtschafts-Archiv, G.m.b.H.

PIWOWARSKY, EUGEN. "*Hochwertiges Gusseisen (Grauguss), seine Eigenschaften und die physikalische Metallurgie seiner Herstellung.*" Zweite, verbesserte Auflage. Pp. xii + 1070. Illustrated. Berlin, Göttingen, Heidelberg, 1951: Springer-Verlag. (Price DM 135.00).

"*Quin's Metal Handbook.*" Thirty-Eighth Year of Publication. Editor: F. B. Rice-Oxley. Sm. 4to, pp. 656. London, 1951: Metal Information Bureau, Ltd. (Price 20*s.*)

SCHIMPKE, PAUL. "*Die neueren Schweissverfahren, mit besonderer Berücksichtigung der Gasschweisstechnik.*" 7. Aufl. Werkstattbücher, H.13. Pp. 61. Illustrated. Berlin, Göttingen, Heidelberg, 1950: Springer-Verlag. (Price DM 3.60)

SCHMIDT, E. "*Einführung in die technische Thermodynamik und in die Grundlagen der chemischen Thermodynamik.*" La. 8vo, pp. xvi + 520. Illustrated. Berlin: Springer-Verlag. (Price DM 30.–)

SIMMONS, WARD F., and HOWARD C. CROSS. "*Report on the Elevated-Temperature Properties of Stainless Steels.*" Issued under the Auspices of the Data and Publications Panel of the ASTM–ASME Joint Committee on Effect of Temperature on the Properties of Metals. Special Technical Publication No. 124. La. 4to, pp. iv + 116. Illustrated. Philadephia, Pa., 1952: American Society for Testing Materials. (Price $4)

"*A Technical Survey of the Abbey, Margam, Trostre and Newport Plants of The Steel Company of Wales, Limited.*" 4to, pp. 312 (+ 266 pp. manufacturers' announcements). London, 1952: Industrial Newspapers, Ltd. (Price 10*s.*)

TRIPP, BASIL H. "*Founded on Fact. An Industry's Service to the Nation.*" 8vo, pp. 45. Illustrated. London, 1952: Council of Ironfoundry Associations.

ZUIDEMA, H. H. "*Performance of Lubricating Oils.* American Chemical Society Monograph No. 113. Pp. 250. Illustrated. New York, 1952: Reinhold Publishing Corporation. (Price $5)

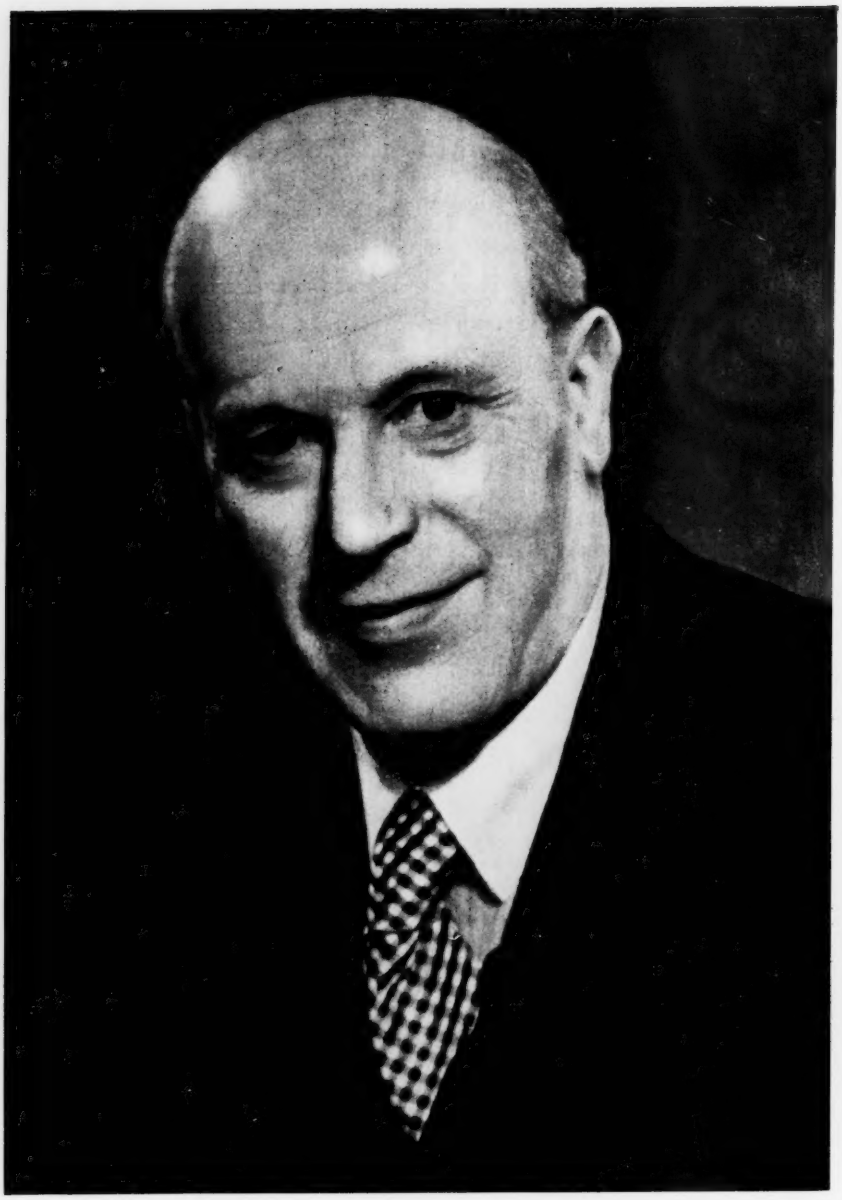
E. N. da C. ANDRADE, D.Sc., Ph.D., LL.D., F.R.S.

PROFESSOR E. N. da C. ANDRADE was born in London in 1887 and was educated at St. Dunstan's College, the Universities of London, Heidelberg, and Manchester, and at the Cavendish Laboratory at Cambridge. He served as an Artillery Officer in France in the 1914-1918 war, and for some years afterwards he was Professor at the Artillery College (later called the Military College of Science). In 1928 he was appointed Quain Professor of Physics in the University of London, and at University College he established a flourishing school of physics, known for fundamental work on the mechanical properties of the solid and liquid state. Since 1st January, 1950, he has been Director in the Royal Institution of Great Britain and Director of the Davy Faraday Research Laboratory.

In the academic field, Professor Andrade has received wide recognition. He was elected a Fellow of the Royal Society in 1935, and in 1948 he was appointed its Honorary Librarian. In addition to the D.Sc. (London) and Ph.D. (Heidelberg), he holds the honorary degrees of LL.D. of the University of Edinburgh and D.Sc. of the University of Durham.

His services to science and to international understanding have been recognized in France by his election as Membre Correspondant de l'Académie des Sciences de l'Institut de France and by the award of the Cross of the Legion d'Honneur. In October, 1951, the Société Francaise de Métallurgie awarded him its Grande Médaille Osmond.

His extensive knowledge of the history of science is widely recognized; he is a leading authority on Newton and delivered in 1949 the Wilkins Lecture of the Royal Society, on Robert Hooke. He is known as a bibliophile. His interests extend also to poetry, art, and music.



Lafayette

E. N. da C. Andrade, D.Sc., Ph.D., LL.D., F.R.S.